

Modeling of Damage in Cement-Based Materials Subjected to External Sulfate Attack. II: Comparison with Experiments

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Abstract: A study is presented to predict the degradation of cement-based materials due to external sulfate attack. Parameters of the model are chosen based on the mix design parameters, degree of hydration, and exposure conditions of concrete. A solution of the diffusion equation with a term for a second-order chemical reaction is proposed to determine the sulfate concentration and calcium aluminate profile as a function of time and space. The crystallization pressure of hydration products such as ettringite can lead to internal stresses. Using the volumetric information, the model predicts the generation of internal stresses, evolution of damage, reduction in stiffness, and thus expansion of a matrix phase. The theoretical expansion-time responses are obtained and compared with a variety of available data in the literature. The most important parameters are the w/c ratio, internal porosity, diffusivity of the cracked and uncracked material, and available calcium aluminates. The importance of controlling the pH of the test solution is clearly observed. Model simulations indicate a reasonable agreement with experimental expansion-time data available in the literature.

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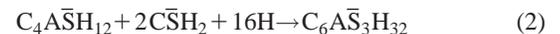
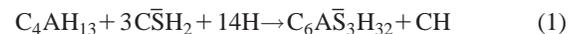
Introduction and Summary of Previous Work

A majority of the durability issues in concrete structures deal with the diffusion of one or several different ions into the material. However, due to the complexity of the different mechanisms involved, a single model predicting a universal response cannot be used. Very few durability models are currently applicable to external sulfate attack, but recent reliability-based theoretical approaches have been developed to estimate the performance of concrete structures (Corr et al. 2000).

Portland cement-based materials subjected to attack from external sulfates may suffer from two types of damage: loss of strength of the matrix due to degradation of C-S-H, and volumetric expansion leading to cracking (Cohen and Mather 1991). Loss of strength has been linked to decalcification of the cement paste hydrates upon sulfate ingress, especially C-S-H, or sulfate attack on C-S-H and CH in the presence of carbonate ions to form thaumasite. The thaumasite formation is accompanied by loss of strength and results in transformation of hardened concrete into a friable mass since a significant part of C-S-H can be destroyed. This process may occur with every type of sulfate salts and is encouraged by humid atmospheres and low temperature (<10°C) (Pauri and Collepari 1989). Expansion, which leads to cracking, is attributed to formation of expansive compounds such as ettringite. Other theories are also proposed to attribute the damage to formation of gypsum crystals (Tian and Cohen 2000). Regardless

of the theory used, the present approach allows for changing the mechanical properties based on both formation of microcracks in the context of damage mechanics and reduction of tensile strength through the use of heuristic and empirically based approaches.

It is possible that the processes of both diffusion and reaction control the sulfate attack mechanism. A detailed derivation of the model proposed, based on the diffusion-reaction approach, is provided in an accompanying publication (Tixier and Mobasher 2003); however, key factors of the model are presented here. Fick's second law is assumed for diffusion of the sulfate ions, and a second-order chemical reaction between penetrating sulfates consumed by reacting with calcium aluminates is considered. The general format of the equation is based on the formation of ettringite from an aluminate phase and the potential expansions associated with that. Three compounds may react with ingressing sulfates (represented in the form of gypsum) according to one of the following reactions:



These reactions are lumped in a global sulfate phase-aluminate phase reaction, as described in the previous part of the paper (Tixier and Mobasher 2003) and represented as $P_i + a_i\bar{S} \rightarrow C_6A\bar{S}_3H_{32}$ where P_i represents the weighted average proportion of the aluminate phase taking part in the reaction, and a_i represents the stoichiometric sulfate required for the reaction, namely, 3, 2, and 3 for Eqs. (1) through (3). Similar to the model by Clifton et al. (1994), the expansion is predicted from the molar volumes of the different components of the cement paste and its microstructural parameters (degree of hydration, capillary porosity) (Clifton and Pommersheim 1994). The crystallization pressure of the products of the reaction results in a bulk expansion of the solid. It is also proposed that no expansion occurs until the capillary pores are totally filled with ettringite. The effect of pore

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filling with ettringite is addressed using a single scalar parameter representing the available volume of pores.

The products of the second-order reaction between the aluminates and sulfates are chosen among several competing mechanisms, and a rule-of-mixtures approach is used to relate the expansive nature of the products to the prescribed specific gravity of the compounds. The initial conditions of the problem, such as the specimen geometry, sulfate exposure, chemical composition of the cement, C_3A content, degree of hydration, and mechanical properties, are specified as the input parameters. The characteristics of concrete, such as the w/c, degree of hydration, and capillary porosity, are also used in the definition of initial variables. The sulfate concentration due to the exposure conditions is specified, and the finite-difference algorithm is initiated to solve the diffusion equation. As the penetration of sulfates takes place, due to reaction with C_3A , sulfate ion concentration is depleted, thus reducing the flux. As the reaction level proceeds, it may be possible that the C_3A levels are depleted, in which case the solution converges to a standard Fick's law solution. If sufficient aluminates are present, then the reaction component of the equation may result in hydration products and reduction of stiffness and strength due to its coupling with the mechanical properties, and also diffusivity. The depth of deterioration at a given time can be correlated with the reacted calcium aluminates content.

A new scalar parameter, f , is defined to take into account the percentage volume of pores that are filled before expansion starts. A value of $f=0$ indicates that no internal porosity is available to take up the volume of expansion products formed. A value of $f=1$ indicates that the entire capillary porosity may be used to accumulate the expansion products before any additional volume would contribute to expansion. The strength parameters include the stiffness E and also the tensile strength f'_t . Additional model parameters include the rate of reaction k and the diffusion coefficient parameter D , which is considered as a function of the damage due to microcracking, ω .

Stresses within the concrete are computed by assuming a specimen as an elastic matrix containing expansive inclusions. The volumetric expansion of the pores containing the reaction products determines the stresses and the damage parameter. Due to the expansion of the sites located within the diffusion front zone, tensile stress fields are generated. The constitutive response of the matrix and the expansive stresses are calculated from the imposed volumetric strains. Microcracks are initiated when the strength of the matrix is reached, which leads to changes in the diffusivity and a reduction in the elastic properties of the matrix. The theoretical expansion-time responses are obtained by integrating the strain as a function of space and obtaining an average strain distribution across the cross section. The variation of diffusivity due to cracking of the matrix is represented as a scalar function of the damage parameter. Due to the changes in the diffusivity, the problem is treated as a moving boundary problem, and the solution methodology is presented in detail.

The following sections present an overview of the existing models for sulfate attack to support the assumptions made in the parametric study. Items of interest include the crystallization pressure of ettringite formation, the diffusion coefficient of sulfates in cement-based materials, and the influence of experimental parameters on the results of expansion tests. The proposed model is applied to test results of several independently conducted experiments available from the literature, including studies of mortar and concrete at various water-to-cement ratios, porosities, and C_3A contents, as well as the presence of mineral admixtures (Rodriguez-Camacho 1998; Mobasher and Arino 1995).

Crystallization Pressure and Damage in Cement-Based Materials

For the case of delayed ettringite formation, thermodynamical considerations have been used to show that the nucleation of ettringite crystals will preferentially occur in the crack tip (Beaudoin et al. 1993; Fu et al. 1994; Fu and Beaudoin 1995). Procedures have been developed to calculate values of crystallization pressure P using a logarithmic form: $P = \beta \ln A$, with term A defined by various authors (Schmidt-Döhl and Rostásy 1995). Based on the Riecke principle, the crystallization pressure of a salt is given as (Winkler 1975):

$$P = \frac{RT}{V_s} \ln \left(\frac{C}{C_s} \right) \quad (4)$$

with R as the ideal gas constant, T as temperature, V_s as molar volume, C as actual concentration of the solute, and C_s as saturation concentration. For ettringite, with a molar weight of 1,252 g and a specific gravity of 1.78 g/cm³, P ranges from 2.4 to 8.1 MPa for a degree of supersaturation C/C_s of 2 to 10, at a temperature of 25°C. Another equation has been proposed using Gibb's free energy (Ping and Beaudoin 1992a, b)

$$P = P_s - P_s^0 = \frac{RT}{V_s} \ln \left(\frac{K_{sp}}{K_{sp}^0} \right) \quad (5)$$

The terms K_{sp} and K_{sp}^0 represent the solubility product of the crystallite under pressure P and P_s^0 (atmospheric pressure) respectively. The value of K_{sp}^0 at 25°C for ettringite varies from $10^{-43.13}$ (Reardon 1990) to $10^{-44.91}$ (Warren and Reardon 1994). Other values can be found in the literature as well (Constantiner and Farrington 1999). According to Ping and Beaudoin (Ping and Beaudoin 1992a), K_{sp}^0 is so low that the condition $K_{sp} > K_{sp}^0$ "can be readily met for practical cement paste/sulfate solution systems," implying that $P > 0$. For ratios of K_{sp}/K_{sp}^0 identical to degrees of supersaturation C/C_s of 2 to 10, at a temperature of 25°C, similar crystallization pressures are obtained. Although no data for K_{sp} at higher pressure are available, one can consider that, even for high K_{sp}/K_{sp}^0 ratios, crystallization pressures of the same order of magnitude can be reached due to the decreasing slope of the logarithm function. Data for K_{sp} as a function of temperature (Perkins and Palmer 1999) indicate that at a temperature of 70°C at which ettringite begins to thermally degrade, the ratio K_{sp}/K_{sp}^0 is equal to 10.8, corresponding to a pressure of 9.7 MPa.

The crystallization pressure of ettringite at 25°C was found equal to 55.5 MPa for portland cement by taking into account the "change of interface energy" (Min and Tang 1994). Another approach to calculating the crystallization pressure based on an expression for the term A , is the ratio of the solubility products of the solid reactants and products. From the formation reaction of ettringite from $C_4A_3\bar{S}$, lime, and gypsum, a value of 71 MPa has been computed for the crystallization pressure (Dron and Brivot 1986).

Internal ettringite formation creates stress concentration at the tip of preexisting cracks (Diamond 1996). If the crystallization pressure is high enough, a single microcrack can propagate incrementally and potentially coalesce with other microcracks in the vicinity. The higher the pressure, the smaller the size of a crack that is able to propagate (Scherer 1999). This relationship is shown in Fig. 1. The stress intensity factor K_I (mode I state) due to the existence of a crack of size c , placed in a large body subjected to a surface load p can be computed from linear elastic fracture mechanics (Murakami 1987) as

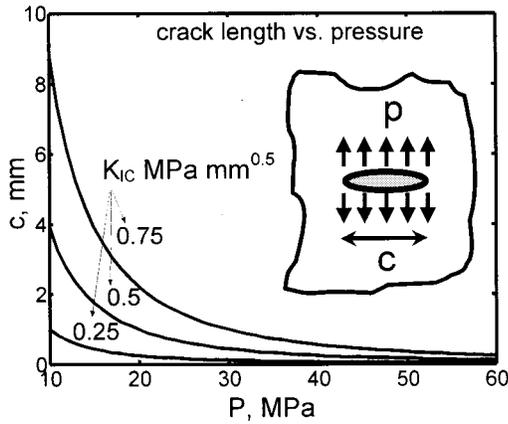


Fig. 1. Schematic representation of crack in infinite medium subjected to surface load

$$K_I = \frac{2p}{\pi} \sqrt{\pi c} \quad (6)$$

As shown in Fig. 1, for a mortar with a classical value for K_{Ic} of $0.5 \text{ MPa}\cdot\text{m}^{1/2}$, the critical size of the crack would be 1.9 mm for $p=10 \text{ MPa}$ but only $64 \mu\text{m}$ for $p=55.5 \text{ MPa}$. Even though the crystallization pressure may not necessarily be uniformly distributed, this rough estimation of the critical size shows that small cracks can propagate under values of p reported in the literature. Depending on the products of reaction, the volumetric ratio of ettringite to calcium aluminates and gypsum are used to compute the relative volume change of paste $\Delta V_p/V_p$ (Tixier and Mobasher 2003). Note that m_v represents the molar volume, p the specific aluminate phase, and “ a ” the stoichiometric proportion of the calcium aluminates and gypsum

$$\left(\frac{\Delta V_p}{V_p}\right) = \frac{1}{\frac{m_v \text{ ettringite}}{a} + m_v \text{ gypsum}} - 1 \quad (7)$$

The values of reacted calcium aluminates are obtained from the differences between initial and current calcium aluminates (C_a) and are used to calculate the volumetric and hydrostatic or uniaxial strain and stress measures shown in Figs. 2 and 3

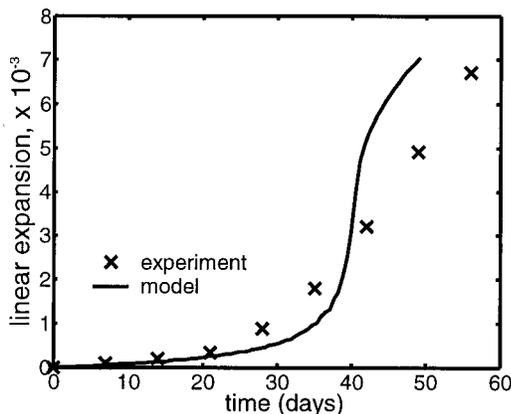


Fig. 2. Validation of model for data by Brown (1981)

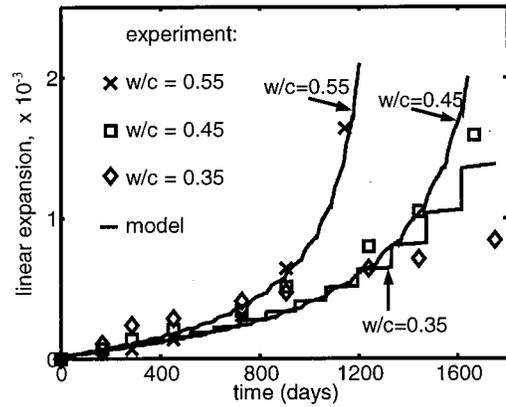


Fig. 3. Validation of model for data by Lagerblad (1999) (concrete—OPC)

$$\varepsilon_v(x,t) = [C_a - C(x,t)] \sum_p \left(\frac{\Delta V}{V}\right)_p \quad (8)$$

$$\sigma_p = K \varepsilon_v \quad \text{where } K = \frac{E}{3(1-2\nu)} \quad (9)$$

Sulfate Diffusivity

Limited data are available on the measurement of sulfate diffusivity in cement-based materials. Widely different experimental conditions and methods, as well as the very limited number of reported values, make it difficult to choose a reasonable value for the diffusivity. Several authors presenting models for sulfate attack have arbitrarily chosen diffusivities between 0.75×10^{-12} and $9 \times 10^{-12} \text{ m}^2/\text{s}$, often with no specific justification. It should be emphasized that reactions between penetrating sulfates and cement paste may profoundly alter the diffusion process; thus the effective diffusivity is likely to be very different from the intrinsic diffusivity (Chatterji 1995). By fitting experimental data to Fick’s law, an “effective diffusivity” D_{eff} parameter is defined (Locoge et al. 1992). Since this value is actually measured, it provides an estimate of the intrinsic diffusivity based on the diffusion-reaction equation.

For a paste with a water/cement (w/c) ratio of 0.30, values of effective diffusivity at different times of curing (various pore-size distributions) range from $4.8 \times 10^{-12} \text{ m}^2/\text{s}$ at 60 days to $1.9 \times 10^{-12} \text{ m}^2/\text{s}$ at 180 days (Gospodinov et al. 1996). At the higher w/c ratio of 0.40, lower values of diffusivity of pastes were reported ranging from 0.6×10^{-14} to $1.34 \times 10^{-14} \text{ m}^2/\text{s}$ at 28 days of exposure (Cabrera and Plowman 1988). This is in apparent contradiction to the values of the pastes previously mentioned.

For a concrete with a w/c ratio of 0.42, cured at 100% relative humidity (RH) for 14 days, the effective sulfate diffusivity was empirically related to the time of exposure to the sulfate solution is represented in Eq. (7) (Tumidajski et al. 1995), with t being the time of exposure in months and D_{eff} the effective sulfate diffusivity in centimeters square per second (cm^2/s). Experimental values range from $4.73 \times 10^{-12} \text{ m}^2/\text{s}$ at 16 months to $1.06 \times 10^{-12} \text{ m}^2/\text{s}$ at 5 years.

$$D_{eff} = 2.217 \times 10^{-7} \times t^{-0.76} \quad (10)$$

The diffusivity in mortars measured using radioactive tracers ranged from 2.7×10^{-14} to 9.5×10^{-14} m^2/s (Spinks et al. 1952). Tests performed on pastes yielded lower diffusion coefficients. No notable difference between Types I and V cements was detected. The diffusivity decreases as a function of time of exposure, with a two-fold decrease between 4 and 12 weeks and a much smaller decrease between 12 and 24 weeks. Based on data obtained through EDXA analyses (Feldman et al. 1989), diffusivity in concrete with w/c ratios from 0.35 to 0.60 and blended or neat binders was calculated (Clifton et al. 1994). Values range from 1.3×10^{-13} m^2/s for a concrete with type I cement and a w/c ratio of 0.50, to 1.7×10^{-15} m^2/s for a concrete with slag cement and a w/c ratio of 0.42.

The following values of the intrinsic sulfate diffusivity for concrete have been reported (Marchand et al. 1999): 1.05×10^{-11} m^2/s for $w/c=0.45$ and 3.54×10^{-11} m^2/s for $w/c=0.65$. Also, taking into account the effect of sulfate attack on the value of the porosity of the cement paste, it was estimated that the diffusivity of a paste can be increased by at least an order of magnitude. Another indirect approach is to relate intrinsic ionic diffusivity D to the water permeability coefficient K . The relation presented by Eq. (8) has been proposed, where A is the cross-sectional area and b is a constant suggested as 1.5 (Nilsson and Luping 1995). The sulfate ion diffusivity represented by Eq. (12) is obtained when this relationship is applied to both chloride and sulfate ions. For the same K and A parameters one obtains

$$K = \frac{A}{8\pi D_f} D^b \quad (11)$$

$$D_{SO_4} = D_{Cl} \left(\frac{D_{fSO_4}}{D_{fCl}} \right)^{2/b} \quad (12)$$

From this expression, it is possible to calculate sulfate diffusivity if D_{Cl} is known and using a value of D_{fCl} at 25°C , equal to 2.03×10^{-9} m^2/s (CRC 1999). For example, regular-strength concrete and mortar with chloride diffusivity ranging from 1×10^{-12} to 10×10^{-12} m^2/s (Tuutti 1982; Kropp 1995) correspond to sulfate diffusivities in the range of 2×10^{-12} to 20×10^{-12} m^2/s .

Effect of Solution pH

Many tests reported in the literature are based on ASTM standard C 1012 with various modifications introduced. Among these modifications, a process that controls the pH of the solution is quite important. The standard test requires that the external sulfate concentration be constant, but it does not take into account the modification of the sulfate solution that occurs when the volume of solution is small compared to the volume of the specimen. It is known that the pH of the solution increases due to outward migration of OH^- ions from the cement paste. In the field, the volume of surrounding solution may be much larger than the structural element considered and constantly renewed, which prevents the pH from changing. Consequently, it has been proposed that the pH of the solution be monitored during the test and adjusted to a constant value by acidic addition (Mehta and Gjorv 1974; Mehta 1975). Results of experiments by Brown (1981) on the effect of pH are shown in Fig. 4. Keeping the pH constant was shown to accelerate the test, both from the loss of strength and the expansion rate, viewpoints. Comparative tests between controlled and uncontrolled pH conditions show that the time to reach a certain level of expansion for the uncontrolled pH condition is

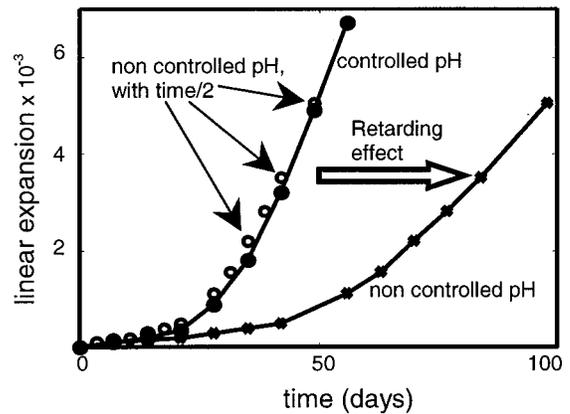


Fig. 4. Effect of pH control on rate of expansion (after Brown 1981)

roughly twice as much as for the controlled pH condition (Brown 1981; Ferraris et al. 1997). Since the migration of OH^- ions is not accounted for in the present model, expansion results from uncontrolled pH tests will be converted to equivalent controlled pH test data by dividing the time scale by a factor of two.

The ASTM C1012 standard prismatic mortar bars have a cross section of 25×25 mm and a gauge length of 250 mm. It was shown that for bars with increasing cross sections, expansion is retarded accordingly. No difference in expansion was noted between 25×25 mm square prisms and 25 mm diameter cylindrical prisms (Ferraris et al. 1997).

Comparison of Model with Experimental Data

Tests under which the pH of the solution is both controlled and uncontrolled were compared with the outputs from the model. The standard solution used in the model for all tests was sodium sulfate, whose concentration was 352 mmol of sulfates/liter of solution. For a classical value of porosity of 10% for a mortar, this concentration is equivalent to $35.2 \text{ mol}/\text{m}^3$ of mortar. No data were readily available from the literature to measure the parameter k , the rate constant of reaction between calcium aluminates and sulfates. A parametric study on the effect of the rate constant was conducted in previous work (Tixier 2000).

Results were indicative that the rate constant is far less effective in changing the diffusion characteristics compared to the diffusivity. A uniform rate constant equal to 10^{-7} $\text{m}^3/\text{mol} \cdot \text{s}$ was therefore used in the remainder of the studies, and the diffusivity was used primarily to simulate the changes in the experimental data. The program was executed until one of the termination criteria was met. These included the maximum time of the experiment, exhaustion of all calcium aluminates, or a maximum expansion magnitude defined by total damage evolution was reached. The initial number of space intervals was 50, representing a resolution of the order of 0.5 mm cell size.

Fig. 5 shows the influence of the value of the fraction of capillary porosity that can be filled with the expansion products (parameter f). Note that the amount of expansive products generated is independent of this parameter; however, increasing it significantly reduces the rate of expansion. When f is increased, it indicates that sufficient internal porosity is made available for the expansion products. Therefore, both the final expansion and the

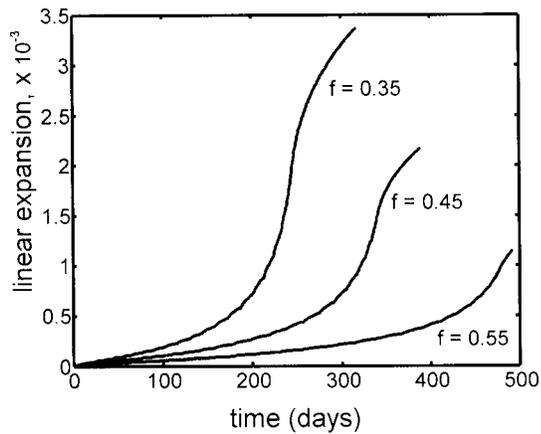


Fig. 5. Effect of value of parameter f on rate of expansion

rate of expansion predicted are reduced. If f is reduced, the volume generated will directly result in generation of internal stresses and this expansion.

The expansion plots shown in Fig. 6 represent the three cases of varying C_3A content for the cement. Three levels of 4, 8, and 12% are studied. These plots clearly indicate the importance of the C_3A content for the magnitude and extent of reaction. The C_3A content of the cement is the main dominating factor in the control of the expansion. Note that it is possible to use the model to compare the expansion of other aluminate phases as well.

Effect of w/c and Capillary Porosity

Samples with a high w/c ratio of 0.60, with a cement at 14% C_3A were used by Brown (1981). The value of the parameters for fitting the data are shown in Fig. 2. Note that as the damage accumulates in the specimen, significant cracking degrades the stiffness, resulting in excessive expansion and deterioration beyond 30 days. This represents the susceptibility of a concrete with a high w/c ratio, low strength, and high C_3A content to the sulfate attack.

Lagerblad (1999) conducted tests on mortar and concrete samples with three different w/c ratios of 0.55, 0.45, and 0.35. The same cement was used for both the mortar and the concrete studies. The tests on concrete specimens were conducted on 75

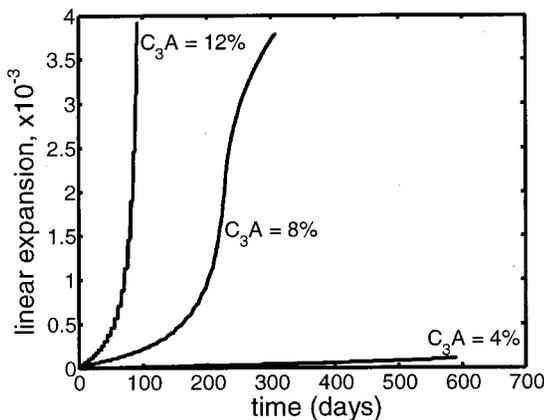


Fig. 6. Effect of cement C_3A content on rate of expansion

Table 1. Parameters Used to Fit Experimental Data [Lagerblad (1999)—concrete]

Cement type	w/c	D_2 (m^2/s)	f	f'_i (MPa)	E_0 (GPa)
OPC	0.55	1×10^{-12}	0.35	3	20
	0.45	5×10^{-13}	0.45	4	22
	0.35	6×10^{-14}	NR	6	25
SRPC	0.55	8×10^{-13}	0.05	3	20
	0.45	5×10^{-13}	0.05	4	22
	0.35	1×10^{-13}	NR	5	24

$\times 75 \times 300$ mm prisms. It should be noted that these prisms are less slender than their mortar counterparts. To enhance the penetration of sulfate ions, they were immersed upright in the solution with their uppermost part left above the surface. This particular boundary condition is not taken into account in the model.

The values chosen for the parameters used to fit the model are displayed in Table 1. Note that as the w/c decreases, the diffusivity is decreased and the tensile strength parameter is increased. Fig. 3 represents the expansion time results of the three different w/c mixes using ordinary portland cement concrete. Note that the samples with the higher porosity responded to the expansive stresses quite a bit faster than the denser concrete specimens. Fig. 7 represents the response of a high w/c ratio sulfate resisting portland cement (SRPC) concrete tested by Lagerblad (1999). Note that in this test the theoretical computations are terminated due to complete consumption of calcium aluminates (C_3A content of 1.2%). The magnitude of expansion remains well below the other magnitudes achieved with the normal portland cement

Effect of Initial C_3A Content

The resistance of plain and blended concrete (C_3A content between 5 and 12%) to sulfate solutions has been studied by several authors (Lizarraga 1997; Rodriguez-Camacho 1998). The effect of the initial C_3A content was studied by evaluating the test results of a series of experiments (Ouyang et al. 1988). Four cements with increasing C_3A content ranging from 4.3 to 12% were used and expansion data were recorded. These tests were not conducted with a controlled pH environment; hence the time scale was divided by two for objectivity of the model and a realistic comparison with experimental data. It is noted that in these ex-

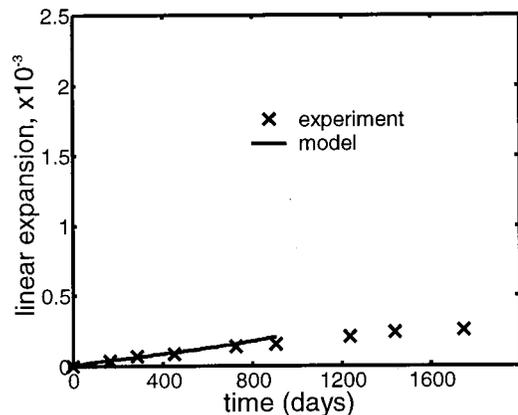


Fig. 7. Validation of model for data by Lagerblad (1999) (concrete—SRPC, $w/c = 0.55$)

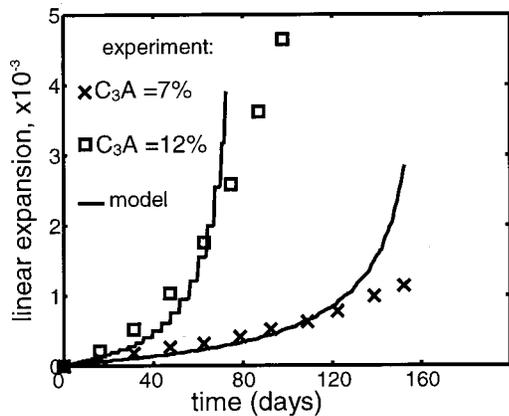
Table 2. Parameters Used to Fit Experimental Data [Ouyang et al. (1988)]

C ₃ A content (%)	D ₂ (m ² /s)	f	f' _t (MPa)	E ₀ (GPa)
4.3	8 × 10 ⁻¹³	0.25	5	20
7.0	7 × 10 ⁻¹³	0.30	5	20
8.8	7 × 10 ⁻¹³	0.30	5	20
12	7 × 10 ⁻¹³	0.35	5	20

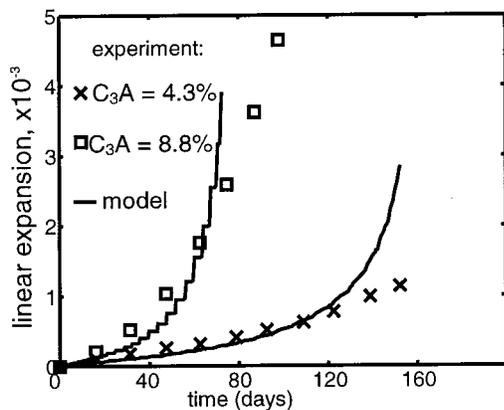
periments only the trends of the data should be considered. The parameters used in the theoretical calculations are reported in Table 2. The results are shown in Figs. 8(a) and (b). Note that as the initial C₃A increases, the expansion also increases as a function of time, no attempt is made to fit the expansion curve results with the theoretical model, and only the trends of the experimental data are simulated.

Tests by Ferraris et al. (1997) used a cement with a high C₃A content of 12.8%. The w/c ratio used was 0.485. The value of the parameters for fitting the data and the expansion time history results are in Fig. 9. A reasonable fit is obtained by adjusting the input data in this case.

An OPC and an SRPC with C₃A contents of 7.7 and 1.2%, respectively, were tested by Lagerblad (1999). Two w/c ratios of 0.485 for both cements and 0.32 for the OPC only were used. The



(a)



(b)

Fig. 8. Validation of model for data by Ouyang et al. (1988): (a) C₃A content of 7 and 12%; (b) C₃A content of 4.3 and 8.8%

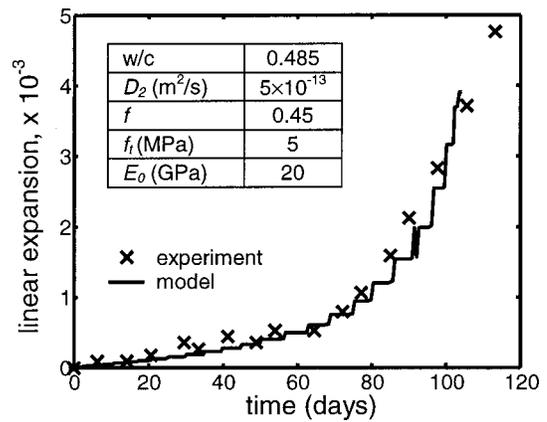


Fig. 9. Validation of model for data by Ferraris et al. (1997)

parameters used to predict the expansion versus time with the model are reported in Table 3, and the results are shown in Fig. 10. Note that in the case of sulfate-resisting concrete mixes, the low dosage of C₃A resulted in a very low expansion magnitude.

Effect of Changes in Diffusivity Due to Use of Mineral Admixtures

It is generally accepted that the use of mineral admixtures such as silica fume, fly ash, or slag significantly improves the sulfate resistance of concrete materials, as verified through experimental tests by various researchers (Hester 1967; Dunstan 1980).

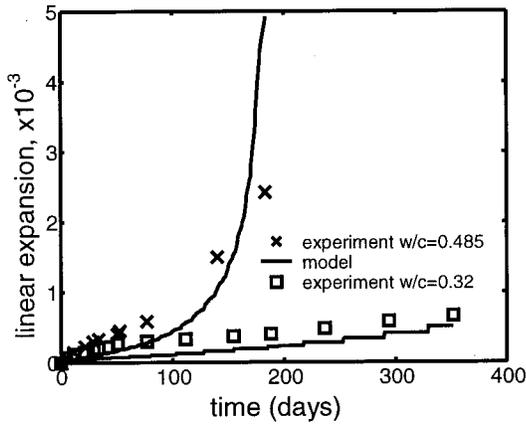
Tests by Mobasher and Ariño (1995) were used to study the effect of copper slag as a mineral admixture. A variable diffusivity parameter was introduced to reflect the use of mineral admixtures in changing the microstructure; these tests were not pH controlled. Test data compare mix designs with and without copper slag for two w/c ratios, 0.40 and 0.50. For the w/c ratio of 0.50, no difference was noted between mortars with or without slag, meaning that, for this w/c ratio, the presence of slag did not significantly modify the physicochemical properties. Alternatively, one can argue that the parameter f representing the internal porosity would be sufficiently high to negate the effect of changes in diffusivity. Hence, only the mortars with a w/c ratio of 0.40 will be compared. Since the type of cement used was ASTM type I, values of 7 and 6% for C₃A and gypsum content were used, respectively.

The parameters corresponding to model-fitting trials and the expansion time histories are shown in Fig. 11. Note that in the case of copper slag, the diffusivity parameter was changed drastically, resulting in a reduction of the expansion.

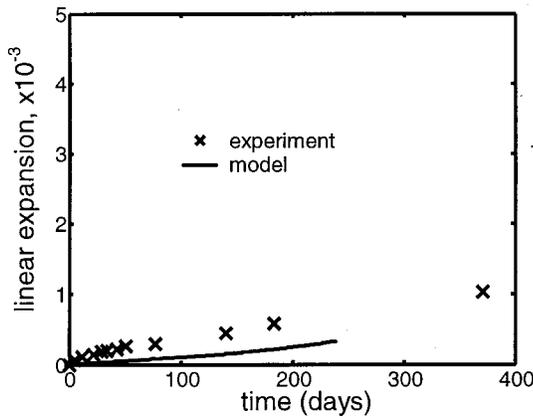
Table 3. Parameters Used to Fit Experimental Data [Lagerblad (1999)—mortars]

Cement type	w/c	D ₂ (m ² /s)	f	f' _t (MPa)	E ₀ (GPa)
OPC	0.485	5 × 10 ⁻¹³	0.3	4.5	20
	0.32	2 × 10 ⁻¹⁴	NR	7	25
SRPC	0.485	5 × 10 ⁻¹³	0.05	4.5	20

Note: NR=not relevant.



(a)



(b)

Fig. 10. Validation of model for data by Lagerblad (1999) (a) mortar—OPC; (b) mortar—SRPC

Effect of Strength and Stiffness Reduction

Monitoring of strength reduction is another measure of detection of damage evolution. In the present work one of the measures of damage evolution is the continuous reduction in the stiffness of the sample. Since the stiffness parameter is used to calculate the expansion of the specimen, it may also be possible to compare the reduction in the apparent Young's modulus as a means of damage evolution. Several sources of data from the literature indicate a possible decrease in the modulus in case of external sulfate attack. Fig. 12 shows the experimental values obtained by Yamato et al. (1989), who measured the dynamic modulus. These data are compared to the values predicted by the model. Unfortunately, no expansion experiments were reported for that study. The parameters of the model are also shown in the figure.

It should be noted that all the parameters D_2 , f , f_t' , and E_0 have been chosen to equal those retained for the fitting of the data on concrete by Lagerblad (1999), $w/c=0.55$; this is because Yamato et al. (1989) used the same w/c ratio. As shown in Fig. 12, the predicted modulus does not match the experimental data very closely, but the trends are quite similar, though it is noted that the natures of the two stiffness measurements are quite different. It would seem that if the experiment had been conducted for a

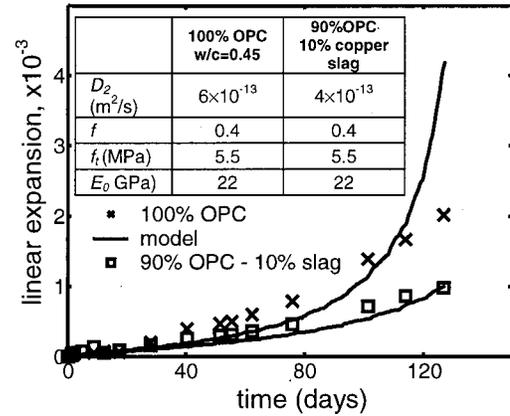


Fig. 11. Validation of model for data by Mobasher and Ariño (1995)

longer period of time, the decaying of the modulus with time would have continued to match the theoretical data.

Discussion

Analysis of the various experimental results indicates that the choice of the values for D_2 (undamaged material diffusivity) is consistent with the w/c ratio of the mix designs, as well as the choice of the values for the mechanical parameters. When all other parameters are kept the same, lower values of w/c lead to a lower diffusivity and hence to a slower expansion rate. This mechanism is clearly predicted by the model.

For a very low C_3A content [Lagerblad (1999) data, mortars and concrete, and SRPC], the potential expansion predicted by the volume change during chemical reactions is very low, which explains why the parameter f had to be chosen much lower than for OPCs. With higher values, no expansion would be predicted because the capillary porosity would be higher than the chemical expansion. In reality, it is known that hydrates from the hydration of C_4AF , while not supposed to be potentially expansive, might still bring about some expansion, although this is not taken into account in the model. This observation is confirmed by the fact that for the SRPC mortar and the SRPC concrete with w/c ratios of 0.55 and 0.45, the model predicts that the reaction ends due to

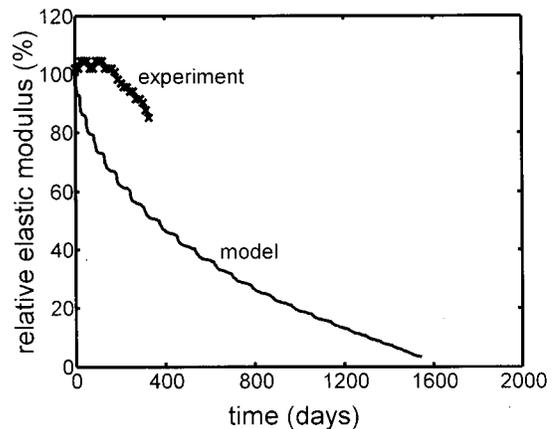


Fig. 12. Validation of model for data by Yamato et al. (1989)

exhaustion of calcium aluminates, before the experimentally measured expansion ceases to increase.

The model also predicts the size effect of the specimen geometry. For comparable w/c ratios (0.485 and 0.45, respectively, for small mortar prisms and large concrete prisms), the same diffusivity and comparable f were used for model prediction. Results indicate that the potential for expansion reduces as the size of the specimen increases. This may be due to the averaging of the specimen size.

Differences in the choice of f may be due to the composition of the cement, which could be related to the internal porosity, the C_4AF content, and also the type of calcium silicate (di-calcium or tri-calcium silicate) responsible for the production of calcium hydroxide. Note that the latter is also involved in the degradation process but, is not taken into account in the model.

Several other parameters may be easily included in the present model as extensions or improvements; such as

- Introduction of the effect of decalcification, especially when magnesium sulfate is present, on the diffusion, the mechanical properties, and the damage parameter ω ;
- Choice of other possible expansion mechanisms such as gypsum formation (as opposed to ettringite formation), resulting in volume change (Brown and Taylor 1999; Tian and Cohen 2000);
- Use of more accurate multiaxial models for the stress-strain-damage response;
- Extension of the diffusivity parameter to incorporate the effect of the interfacial transition zone for mortars and concrete and changes due to the use of blended cements (Garboczi and Bentz 1997); and
- Generalization to the boundary conditions to handle cases of cyclic wetting and drying.

In lieu of the above, more experimental work is needed to address the design of performance tests and understanding of microstructural changes during external sulfate attack in terms of measurement of both physical (expansion, crack density) and mechanical parameters (strength, modulus, fracture parameters) during a performance test. Further areas of need include

- Determination of the intrinsic sulfate diffusivity for various mix designs and binder nature;
- Quantification of the role of C_4AF in the degradation process and of the importance of the C_3S/C_2S content;
- Confirmation of the nature and stoichiometry of the reactions taking place during sulfate attack; and
- Determination of the location and the effect of ettringite formation.

Conclusions

This paper applies a theoretical model to predict the degradation due to external sulfate attack on cement-based materials. From several expressions of the crystallization pressure of ettringite, it can be assumed that ettringite formation can lead to crack propagation. Simulations with the model described in Part 1 Tixier and Mobasher (2003) indicate reasonable agreement with experimental expansion data. Parameters of the model are chosen to be compatible with the actual mix design of the materials. The importance of controlling the pH of the test solution is verified by comparing the experimental and theoretical data. The most important discrepancies observed for very low C_3A , are attributed to the effects of calcium ferro-aluminates and the role of internal porosity in suppressing the expansions.

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Notation

The following symbols are used in this paper:

- A = cross-sectional area;
- a = stoichiometric coefficient of gypsum in ettringite forming reaction;
- b = constant;
- C = concentration;
- C_a = initial molar concentration in calcium aluminates;
- C_s = saturation concentration;
- c = size of microcrack;
- D = diffusivity;
- D_{eff} = effective diffusivity;
- D_f = diffusivity of given ion in pure water;
- D_2 = diffusion coefficient of noncracked material;
- E = elastic modulus of damaged material;
- E_0 = initial elastic modulus of undamaged material;
- f = fraction of capillary porosity being filled by secondary reaction;
- f'_t = ultimate tensile strength;
- $K = E/3(1 - 2\nu)$ [Eq. (9)];
- K = water permeability coefficient [Eq. (11)];
- K_I = stress intensity factor;
- K_{sp} = solubility product;
- k = rate constant of reaction;
- m_v = molar volume;
- P = crystallization pressure;
- p = surface load applied to microcrack;
- R = ideal gas constant;
- T = temperature;
- t = time;
- V_s = molar volume;
- $\Delta V_p/V_p$ = volumetric change;
- ε_v = volumetric strain;
- ν = Poisson's ratio;
- σ_p = uniaxial stress; and
- ω = damage scalar parameter.

References

- Beaudoin, J. J., Fu, Y., Xie, P., and Gu, P. (1993). "Preferred nucleation of secondary ettringite in pre-existing cracks of steam-cured cement paste." *J. Mater. Sci. Lett.*, 12, 1864–1865.
- Brown, P. W. (1981). "An evaluation of the sulfate resistance of cements in a controlled environment." *Cem. Concr. Res.*, 11, 719–727.
- Brown, P. W., and Taylor, H. F. W. (1999). "The role of ettringite in external sulfate attack." *Materials science of concrete: Sulfate attack mechanisms*, J. Marchand and J. P. Skalny, eds., American Ceramic Society, Westerbroke, Ohio, 73–97.
- Cabrera, J. G., and Plowman, C. (1988). "The mechanism and rate of attack of sodium sulfate solution on cement and cement/pfa pastes." *Adv. Cem. Res.*, 1(3), 171–179.

- Chatterji, S. (1995). "On the applicability of Fick's second law to chloride ion migration through portland cement concrete." *Cem. Concr. Res.*, 25(2), 299–303.
- Clifton, J. R., Bentz, D. P., and Pommersheim, J. M. (1994). "Sulfate diffusion in concrete." *NISTIR 5361*, NIST, Gaithersburg, Md.
- Clifton, J. R., and Pommersheim, J. M. (1994). "Sulfate attack of cementitious materials: Volumetric relations and expansions." *NISTIR 5390*, NIST, Gaithersburg, Md.
- Cohen, M. D., and Mather, B. (1991). "Sulfate attack on concrete—Research needs." *ACI Mater. J.*, 88(1), 62–69.
- Constantiner, D., and Farrington, S. A. (1999). "Review of the thermodynamical stability of ettringite." *J. Cem., Concr., Aggregates (ASTM)*, 21(1), 39–42.
- Corr, D. J., Monteiro, P. J. M., Kurtis, K. E., and Kiureghian, A. D. (2000). "Sulfate attack of concrete: Reliability analysis." *ACI Mater. J.*, 98(2), 99–104.
- CRC handbook of chemistry and physics.* (1999). CRC Press, Cleveland, Ohio.
- Diamond, S. (1996). "Delayed ettringite formation—Processes and problems." *Cem. Concr. Compos.*, 18(3), 205–215.
- Dron, R., and Brivot, F. (1986). "A contribution to the study of ettringite caused expansion." *Int. Congress on the Chemistry of Cement*, 5, 115–120.
- Dunstan, Jr., E. R. (1980). "A possible method for identifying fly ashes that will improve sulfate resistance of concrete." *J. Cem., Concr., Aggregates (ASTM)*, 2(1).
- Feldman, R. F., Beaudoin, J. J., and Philipose, K. E. (1989). "Durable concrete for a waste repository—Measurement of ionic ingress." *Scientific basis for nuclear waste management XIII*, V. M. Oversby and P. W. Brown, eds., Materials Research Society, Pittsburgh, 129–142.
- Ferraris, C. F., Clifton, J. R., Stutzman, P. E., and Garboczi, E. J. (1997). "Mechanisms of degradation of portland cement-based systems by sulfate attack." *Mechanisms of chemical degradation of cement-based systems*, K. L. Scrivener and J. F. Young, Eds., E & FN Spon, London, 185–192.
- Fu, Y., and Beaudoin, J. J. (1995). "A through solution mechanism for delayed ettringite formation in pre-existing cracks in portland cement mortar." *J. Mater. Sci. Lett.*, 14, 217–219.
- Fu, Y., Xie, P., Gu, P., and Beaudoin, J. J. (1994). "Significance of pre-existing cracks on nucleation of secondary ettringite in steam-cured cement paste." *Cem. Concr. Res.*, 24(6), 1015–1024.
- Garboczi, E. J., and Bentz, D. P. (1997). "Analytical formulas for interfacial transition zone properties." *Adv. Cem. Based Mater.*, (6), 99–108.
- Gospodinov, P., Kazandjiev, R., and Mironova, M. (1996). "Effect of sulfate ion diffusion on the structure of cement stone." *Cem. Concr. Compos.*, 18(6), 401–407.
- Hester, J. A. (1967). "Fly ash in roadway construction." *Proc., 1st Ash Utilization Symp., Information Circular No. 8348*, U.S. Bureau of Mines, Washington, D.C., 87–100.
- Kropp, J. (1995). "Chlorides in concrete." *Performance criteria for concrete durability*, J. Kropp and H. K. Hilsdorf, eds., E & FN Spon, London, 139–164.
- Lagerblad, B. (1999). "Long term test of concrete resistance against sulphate attack." *Materials science of concrete: Sulfate attack mechanisms*, J. Marchand and J. P. Skalny, eds., American Ceramic Society, Westerbork, Ohio, 325–336.
- Lizarraga, S. (1997). "Behaviour of ash-containing cements in the presence of sulfates." *Cemento Hormigon*, 68(771), 580–602 (*Chem. Abs.* 127,165742).
- Locoge, P., Massat, M., Ollivier, J. P., and Richet, C. (1992). "Ion diffusion in microcracked concrete." *Cem. Concr. Res.*, 22(2–3), 431–438.
- Marchand, J., Samson, E., and Maltais, Y. (1999). "Modeling microstructural alterations of concrete subjected to sulfate attack." *Materials science of concrete: Sulfate attack mechanisms*, J. Marchand and J. P. Skalny, eds., American Ceramic Society, Westerbork, Ohio, 211–257.
- Mehta, P. K. (1975). "Evaluation of sulfate resistance of cements by a new test method." *ACI J.*, 72(10), 573–575.
- Mehta, P. K., and Gjorv, O. E. (1974). "New test for sulfate resistance of cements." *J. Test. Eval.*, 2(60), 510–515.
- Min, D., and Minshu, T. (1994). "Formation and expansion of ettringite crystals." *Cem. Concr. Res.*, 24(1), 119–126.
- Mobasher, B., and Ariño, A. M. (1995). "Durability of copper slag concrete." *Technical Rep. 95-1*, Arizona State University, Tempe, Ariz.
- Murakami, Y., ed. (1987). *Stress intensity factors handbook*, Pergamon, Oxford, (Oxfordshire), U.K.
- Nilsson, L.-O., and Luping, T. (1995). "Relations between different transport parameters." *Performance criteria for concrete durability*, J. Kropp and H. K. Hilsdorf, eds., EE & FN Spon, London, 15–32.
- Ouyang, C. S., Nanni, A., and Chang, W. F. (1988). "Internal and external sources of sulfate-ions in portland-cement mortar—Two types of chemical attack." *Cem. Concr. Res.*, 18(5), 699–709.
- Pauri, M., and Collepardi, M. (1989). "Thermo-hygro-metrical stability of thaumasite and ettringite." *Il Cemento*, 86, 177–184.
- Perkins, R. B., and Palmer, C. D. (1999). "Solubility of ettringite (Ca₆[Al(OH)₆]2(SO₄)₃26H₂O) at 5–75°C." *Geochim. Cosmochim. Acta*, 63(13–14), 1969–1980.
- Ping, X., and Beaudoin, J. J. (1992a). "Mechanism of sulfate expansion. 1: Thermodynamic principle of crystallization pressure." *Cem. Concr. Res.*, 22(4), 631–640.
- Ping, X., and Beaudoin, J. J. (1992b). "Mechanism of sulfate expansion. 2: Validation of thermodynamic theory." *Cem. Concr. Res.*, 22(5), 845–854.
- Reardon, E. J. (1990). "An ion interaction-model for the determination of chemical-equilibria in cement water-systems." *Cem. Concr. Res.*, 20(2), 175–192.
- Rodriguez-Camacho, R. E. (1998). "Using natural pozzolans to improve the sulfate resistance of cement mortars." *Fly ash, silica fume, slag, and natural pozzolans in concrete*, 6th CANMET/ACI/JCI Conf., 1021–1040.
- Scherer, G. W. (1999). "Crystallization in pores." *Cem. Concr. Res.*, 29(8), 1347–1358.
- Schmidt-Döhl, F., and Rostásy, F. S. (1995). "Crystallization and hydration pressure or formation pressure of solid phases." *Cem. Concr. Res.*, 25(2), 255–256.
- Spinks, J. W. T., Baldwin, H. W., and Thorvaldson, T. (1952). "Tracer studies of diffusion in set portland cement." *Canadian Journal of Technology*, 30(1), 20–28.
- Tian, B., and Cohen, M. D. (2000). "Does gypsum formation during sulfate attack on concrete lead to expansion?" *Cem. Concr. Res.*, 30(1), 117–123.
- Tixier, R. (2000). "Microstructural development and sulfate attack modeling in blended cement-based materials," PhD dissertation, Arizona State Univ., Tempe, Ariz.
- Tixier, R., and Mobasher, B. (2003). "Modeling of damage in cement-based materials subjected to external sulfate attack. I: Formulation." *J. Mater. Civ. Eng.*, 15(4).
- Tumidajski, P. J., Chan, G. W., and Philipose, K. E. (1995). "An effective diffusivity for sulfate transport into concrete." *Cem. Concr. Res.*, 25(6), 1159–1163.
- Tuutti, K. (1982). *Corrosion of steel in concrete*, Swedish Cement and Concrete Research Institute, Stockholm.
- Warren, C. J., and Reardon, E. J. (1994). "The solubility of ettringite at 25°C." *Cem. Concr. Res.*, 24(8), 1515–1524.
- Winkler, E. M. (1975). *Stone—Properties, durability in man's environment*, Springer, New York.
- Yamato, T., Soeda, M., and Emoto, Y. (1989). "Chemical resistance of concrete containing condensed silica fume." *Fly ash, silica fume, slag, and natural pozzolans in concrete*, Proc., 3rd Int. Conf., V. M. Malhotra, ed., American Concrete Institute, Detroit, 2, 897–911.