Sulfate Attack of Cementitious Materials: Volumetric Relations and Expansions

James R. Clifton
James M. Ponnersheim*

April 1994
Building and Fire Research Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899

* Bucknell University
  Lewisburg, PA 17837

Sulfate Attack of Cementitious Materials:
Volumetric Relations and Expansion

James M. Pommersheim
Bucknell University
Lewisburg, PA

James R. Clifton
National Institute of Standards and Technology
Building Materials Division
Gaithersburg, MD

Abstract

A model was developed which predicts the conditions under which volumetric expansion of cementitious materials are most likely and the amount of expansion expected. Model parameters include concrete composition, phase densities, water-cement ratio, degree of hydration, extent of expansive reaction and reaction stoichiometry. The model was applied to several different reactions involving sulfate attack of concrete, including gypsum and ettringite formation reactions. The model predicted that ettringite formation from monosulfate would not cause general expansion. However, local expansion could occur if ettringite occupied the same space vacated by reacting monosulfate. The model predicted that if sufficient unhydrated tricalcium aluminate (C_3A) was available in mature cement paste and it reacted with gypsum to form ettringite, the reaction could cause expansion at low water-to-cement ratios.

TABLE OF CONTENTS

LIST OF TABLES AND FIGURES

1. INTRODUCTION

The U.S. Nuclear Regulatory Commission (NRC) his responsibile for developing a strategy to dispose of low-level radioactive wastes (LLW). LLW are to be placed in concrete vaults which are either buried in the earth or constructed above ground and covered with earth. A service life of 500 years is required for the disposal vaults. The National Institute of Standards and Technology (NIST) is carrying out research projects for the NRC aimed at developing performance criteria for the concrete used in constructing the vaults. These criteria are based on service life predictions which take into consideration processes that are likely to degrade concrete located underground.

The major degradation processes that the concrete is likely to encounter are sulfate attack, corrosion of reinforcing steel, alkali-aggregate reactions, carbonation, and leaching by neutral or acidic groundwaters [1]. These degradation processes often involve the transport of moisture, ions and dissolved gases into concrete by diffusion, convection and capillary forces. Rates of degradation will often be controlled by the rate of intrusion of moisture and dissolved salts and gases into concrete.

Sulfate attack is potentially one of the most damaging degradation mechanisms. It can be accelerated in several ways. Alternate cycles of wetting and drying can concentrate soluble sulfates at the exterior faces of concrete members. Hydraulic flow of sulfate solutions from the exterior can augment the inherently slow diffusion of sulfate ions. The expansive nature of the products formed from the reaction between sulfate ions and the aluminate phases of cement may cause cracking of the concrete. Cracking can significantly increase both the diffusion rate and hydraulic flow rate since both the amount of free surfaces and connectivity of the concrete pore structure are increased.

In groundwater and clayey soils, alkali and alkali-earth sulfates can be naturally present. They can be concentrated there by evaporation on repeated irrigation or natural wetting and drying cycles. It is well known [2] that sulfate-bearing waters can attack concrete structures. Over time sulfate attack can cause cracking and even disintegration of concrete members. The potential acceleratory nature of sulfate attack is particularly invidious. The crack network which develops can raise both the permeability and diffusivity, greatly reducing the useful life of the structure. If ground or soil waters surrounding concrete vaults contain an appreciable amount of sulfate, the damage sustained over several hundred years may compromise the chemical and structural integrity of the vault.

In this report a model is developed which predicts the volumetric

expansion of cementitious materials as a function of the specific expansive chemical reaction, degree of reaction, the composition of the concrete, and the densities of the individual phases. The model is based on the concept of excluded volume, whereby, the amount of expansion is presumed to be proportional to the difference between the net solid volume produced and the original capillary porosity.

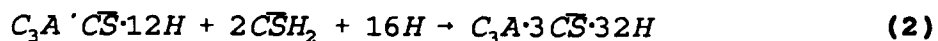## 2. VOLUMETRIC EXPANSION AND CHEMICAL REACTIONS

A number of different reactions have the potential of causing volumetric expansion when cementitious materials are exposed to sulfates in an open system. A potential for expansion exists when the volume of solid products is greater than that of the solid reactants. To quantify this effect, we define an expansion factor v as:

$$v = \frac{solid\ product\ volume\ -\ solid\ reactant\ volume}{solid\ reactant\ volume} \qquad (1)$$

The expansion factor will only depend on the stoichiometry of the reaction. It is independent of the degree of reaction.

Expansion may occur when the volume of solid product is greater than the volume of solid reactants (v > 0). Whether expansion actually occurs or not will depend on the capacity of the cement pore structure to accommodate the expansion as well as the concrete's ability to resist expansive stresses.

To illustrate the calculation of v consider the formation of ettringite ($C_3A \cdot 3C\bar{S} \cdot 32H$) from the reaction between calcium aluminate monosulfate ($C_3A \cdot C\bar{S} \cdot 12H$), and gypsum ($C\bar{S}H_2$)[1]:

$$C_3A \cdot C\bar{S} \cdot 12H + 2C\bar{S}H_2 + 16H \rightarrow C_3A \cdot 3C\bar{S} \cdot 32H \qquad (2)$$

Monosulfate, gypsum and ettringite are all presumed to be present as solid phases. Table 1 gives a listing of the densities and molar volumes of these and related solids [3].

Using the data from Table 1 in solving eq. (1):, v for the reaction given in eq. (2) is:

---

[1]Conventional cement chemistry nomenclature is employed: C = CaO, A = Al_2O_3, F = Fe_2O_3, H = H_2O, $\bar{S}$ = SO_3 and S = SiO_2.

2

$$v = \frac{(3.2/1.4)}{1 + [2(3.2)/13.5]} - 1 = 0.55 \qquad\qquad (3)$$

Table 1. Densities of Cementitious Compounds [3]

Compound	Density (g/cm^3)	Molar Volumes (cm^3)
C_3A	3.04	11.2
$C\bar{S}H_2$	2.32	13.5
CH	2.24	30.2
$H(H_2O)$	1.00	55.5
$C_3A \cdot C\bar{S} \cdot 12H$	1.95	3.20
$C_3A \cdot 3C\bar{S} \cdot 32H$	1.75	1.40
C_4AH_{19}	1.80	2.69
C_4AH_{13}	2.02	3.60
C_3S	3.21	14.1
C_2S	3.28	19.1
$C_{1.7}SH_4$ (cement gel)	1.85	8.06
C_3AH_6	2.52	6.66

This calculation shows there is a 55% volume increase when monosulfate is converted to ettringite. If the gypsum ($C\bar{S}H_2$) were not present as a solid the corresponding volume increase would be 129%.

Table 2 summarizes the volumetric expansion factors for a number of different reactions, most involving sulfate. The principal hydration reactions for tricalcium silicate (C_3S) and dicalcium silicate (C_2S) are shown for comparison, as reactions (H) and (I), respectively. Since v is positive for almost all of the reactions given, each reaction potentially can cause expansion, with the greatest potential existing for those reactions having the higher values of v.

Table 2. Volumetric Expansion Factors, v, and Reactant Ratios, b, for Some Cement Chemical Reactions

Reaction	Chemical Reaction	Expansion Factor, v	Reactant Ratio, b
(A)	$C_3A \cdot C\bar{S} \cdot 12H_2(s) + 2\ C\bar{S}H_2\ (s) + 16\ H = C_3A \cdot 3CS \cdot 32H(s)$	0.55	1.47
(B)	$C_3A\ (s) + 3\ C\bar{S}H_2(s) + 26H = C_3A \cdot 3C\bar{S} \cdot 32H(s)$	1.31	3.49
(C)	$Na_2SO_4\ (aq) + CH\ (s) + 2\ H = 2NaOH\ (aq) + C\bar{S}H_2(s)$	1.24	1
(D)	$C_3A\ (s) + 3\ Na_2SO_4(aq) + 3\ CH(s) + 32\ H = 6NaOH\ (aq) + C_3A \cdot 3C\bar{S} \cdot 32H(s)$	2.83	2.11
(E)	$3\ C_3A \cdot C\bar{S} \cdot H_{12}\ (s) + 3\ Na_2SO_4(aq) = 6NaOH\ (aq) + 2\ Al(OH)_3(aq) + 21\ H + 2\ C_3A \cdot 3C\bar{S} \cdot 32H(s)$	0.52	1
(F)	$C_3AH_6(s) + 3C\bar{S}H_2(s) + 20\ H = C_3A \cdot 3C\bar{S} \cdot 32H(s)$	0.92	2.48
(G)	$C_3A \cdot 3C\bar{S} \cdot 32H(s) + 2\ C_3A(s) + 4\ H = 3\ C_3A \cdot C\bar{S} \cdot 12H(s)$	−0.05	5.00
(H)	$C_3S\ (s) + 5.3\ H = 1.3\ CH\ (s) + C_{1.7}SH(s)$	1.35	1
(I)	$C_2S\ (s) + 4.3\ H = 0.3\ CH\ (s) + C_{1.7}SH_4(s)$	1.56	1
(J)	$C_3A(s) + 6H = C_3AH_6(s)$	0.68	1

The formation of ettringite from tricalcium aluminate (C_3A) and gypsum ($C\bar{S}H_2$) via reaction in eq. (2), has a volume increase of 131%. Because this reaction occurs before the microstructure of the cement is fully developed and the cement has a low modulus of elasticity, the volume increase can usually be accommodated. However, at later times, if previously inaccessible C_3A becomes exposed to sulfate solutions, the volume increase may not be able to be accommodated and expansion may result. Excessive expansion may cause cracking which can expose more unreacted C_3A to the sulfate solutions.
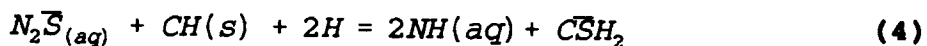
Figure 1 depicts the volume changes which occur due to reactions

(B)and C of Table 2. A volume unit of C_3A reacts with 2.5 units of gypsum and 5.3 units of water to form 8.1 volume units of ettringite. If the gypsum in reaction (B) is formed via reaction (C) then 1.1 volume units of calcium hydroxide is needed to produce it.

Ettringite also can be formed directly when calcium aluminate hydrates such as C_3AH_6 react with gypsum and additional sulfate ions via reaction (F). This reaction is more expansive than the conversion of monosulfate to ettringite. Calcium aluminate hydrates form when the C_3A phase hydrates, while the monosulfate is formed within concrete when the sulfate concentration in the pore solution drops to a point where it is insufficient to stabilize ettringite [4,5]. This shifts the equilibrium in reaction (A) to the left, promoting the formation of monosulfate. Monosulfate can also form directly from ettringite and C_3A via reaction (G), a reaction which involves only a small volume decrease. Shrinkage of the cement matrix by ettringite decomposition would be unlikely to cause any significant cracking because during this period the cement paste would have a low modulus of elasticity.

Re-exposure of monosulfate to sulfate solutions at later times, however, could cause significant expansion and possible cracking. Newly formed cracks would imbibe more sulfate by capillarity. Some of the ettringite formed via reactions (A) possibly could cause expansion if formed is the space previously occupied by the monosulfate. Ettringite crystals forming in open spaces, which can easily accommodate them, would not likely to cause expansion. Some pore infilling would also occur by hydration via reactions (H, I, and J) when previously inaccessible, unreacted C_3S, C_2S, and C_3A were exposed to water by an advancing crack.

nson and Hearne [6] studied the expansion of mortar bars :h were exposed to solutions of sodium sulfate. When :ntitious materials are exposed to external sulfate ɛ ıtions, e.g., sodium sulfate, gypsum is formed via the double deːomposition reaction:

$$N_2\bar{S}_{(aq)} + CH(s) + 2H = 2NH(aq) + C\bar{S}H_2 \qquad (4)$$

The presence of sodium hydroxide will lower the solubility of calcium hydroxide through the common ion effect [7]. However, since the reaction is ionic it still should be fairly rapid. The formation of gypsum will be limited by the diffusion rate of sulfate ions into the cement or concrete [8]. This is a relatively slow process, which becomes slower as the sulfate diffuses deeper into the interior of the concrete [9].

With diffusion control a moving interface will develop between a zone containing calcium hydroxide and a zone where calcium

hydroxide has been replaced by gypsum via reaction (C) with a net expansion of 124%. Although this expansion is relatively high and a moving interface will localize gypsum deposition, it appears to be, in general, accommodated within the pore structure. Gypsum crystals which grow across pores will exert some stress on the pore walls. However, since the modulus of elasticity of gypsum is less than that of concrete, its formation will be unlikely to cause much expansion.

When the gypsum is under stress the crystallization pressure will cause it to redissolve [10] giving higher ion concentrations. This creates a diffusion gradient so that calcium and sulfate ions can diffuse away from the stressed region, promoting crystal growth in adjacent areas. This mechanism will distribute the applied force over a wider area, thus, lowering the effective stress density on the pore walls.

Ettringite crystal growth can occur by the same mechanism. However, there are several important differences as compared to gypsum formation. Ettringite is thought to expand chiefly by water adsorption on its surface, incorporating 32 molecules of water into its crystal structure [11]. Gypsum, on the other hand, only incorporates two water molecules. Ettringite crystals can form as microcrystalline needles from 1-2 μm long and 0.1-0.2 μm thick (aspect ratio ~10) but also can form prismatic crystal habit typical of gypsum [12,13]. The crystal habit of both ettringite and gypsum is strongly affected by the environment in which it forms [12,14]. Ettringite crystals can exert substantial stresses because of their small tip area. In addition, it has been postulated that the gypsum will soften the cement gel, lowering its strength and elastic modulus and making it more susceptible to damage due to ettringite growth [15].

3. MATHEMATICAL MODEL FOR VOLUMETRIC EXPANSION

In this section a mathematical model is developed which predicts the volumetric expansion of cementitious compounds which are exposed to sulfate solutions. The model is based on the potential for expansion provided by both the C_3A content of the cement and the sulfate ion concentration of penetrating aqueous solutions. It also considers the amount of cement in concrete and the characteristics of pores in which the expansive products of the reactions can grow.

Consider a concrete which contains a volume fraction f_c of cement. Let the mass ratios of aggregate (s) to cement (c), water (w) to cement, and entrained air (a) to cement be (s/c), (w/c) and (a/c), respectively. Then a combined volume and mass balance on the concrete yields:

$$f_c = \left[1 + \frac{\rho_c}{\rho_s}\left(\frac{s}{c}\right) + \frac{\rho_c}{\rho_w}\left(\frac{w}{c}\right) + \frac{\rho_c}{\rho_a}\left(\frac{a}{c}\right) \right]^{-1} \qquad (5)$$

where ρ_s, ρ_c, ρ_w, and ρ_a are the densities of the aggregate, cement, water and air, respectively. For a mortar with no air entrainment (a/c) = 0. The aggregate properties of the mortar are those of the sand. An obvious extension of eq. (5) would allow the inclusion of mineral admixtures such as fly ash and silica fume.

Within cement itself it is the tricalcium aluminate and its products reacting with sulfate which provide most of the potential for expansion. Expansion is harmful once the cement has become relatively rigid. Prior to this time the concrete mass actually shrinks as the hydration reactions remove water from both pores and interstitial regions [16]. Since immature concrete has a low modulus of elasticity, it can accommodate expansive stresses. After setting, under continued hydration, the internal porosity of the hardened cement decreases [17].

The volume fraction of C_3A within cement is given by:

$$f_{C_3A} = w_{C_3A}\ \rho_c/\rho_{C_3A} \qquad (6)$$

where
w_{C3A} = weight fraction of C_3A in cement and
ρ_{C_3A} = density of C_3A (3.04 g/cm^3)

A mature cement paste consists of solid hydration products, some unhydrated cement, and capillary and gel pores. In concrete, aggregate particles are also present together with some additional pores created at the paste-aggregate interface. Gel pores are typically less than 4 nm in size and have a relatively narrow pore size distribution, while capillary pores are greater than 4 nm and come in a broad range of sizes [18]. Paste-aggregate pores are of comparable size to capillary pores [19]. The conductance of gel pores is only about 1/400 that of capillary pores [20]. Thus both the diffusivity and permeability of the gel pores will be correspondingly lower and most transport will occur in the capillary pores. The principal mechanisms for transport are mainly by diffusion and convection [21].

The amount of porosity in hydrated portland cement paste from gel pores at around 28-29 percent, while the porosity of the capillary pores varies depending on the water to cement ratio (w/c) and the degree of hydration [16,22]. The connectiveness of the pore network is an important factor in the movement of dissolved salts in cement paste. For (w/c) < 0.57 simulation studies have shown that the capillary pore space is no longer

7

continuous (does not percolate) once a critical degree of hydration is reached [23]. For example, when (w/c) = 0.45 the critical degree of hydration is 76% and the percolation threshold corresponds to a capillary porosity of 18 percent [23].

Since the gel pores are too small to accommodate them, ettringite and other potentially expansive products grow only in the capillary pores and aggregate-cement paste interfacial zones [5]. Veins of gypsum have been observed at the aggregate-cement interface of concrete specimens exposed to sulfate solutions [9].

Since ettringite grows principally in the capillary pores, the potential expansion will depend on the ratio r of the volume of the capillary pores to the total pore volume (gel and capillary pores). This ratio in turn will depend on the (w/c) ratio and the degree of hydration (α) of the cement:

$$r = \frac{(w/c) - 0.39\alpha}{(w/c) - 0.21\alpha} \qquad (7)$$

Eq. (7) is based on the work of Hogland [22]. It is also in substantial agreement with the work of Gieker [16] and Bentz and Garboczi [23]. In simulation studies of a hydrating cement paste Bentz and Garboczi [20] found that the final degree of hydration increased from 0.80 to 0.91 as the (w/c) ratio increased from 0.35 to 0.60. Based on their values, Table 3 gives the value of r calculated from equation (7).

The table shows that as the (w/c) ratio decreases, a smaller fraction of capillary pores are present. Thus less of the total pore structure will be subject to the action of expansive forces. This is another reason for preferring concrete made with low (w/c) cement in addition to the advantages provided by lower permeability and diffusivity. Because of these factors, less expansion is expected for concretes which have been cured longer. Thus, low values of r are desirable.

The last column in Table 3 gives the capillary pore ratio (r_u) at a degree of hydration equal to half of the final value ($\alpha = \alpha_f/2$). The pore ratio is higher when the degree of hydration is less, ranging from 73 to 84%. This comparison points out the importance of properly curing concrete before exposing it to sulfates.

Table 3. Capillary Pore Ratio (r) at Different Water-to-Cement (w/c) Ratios and Final Degrees of Hydration (α_f)[*]

(w/c)	α_f	r_f	$r_{1/2}$
0.35	0.80	0.21	0.73
0.40	0.84	0.32	0.76
0.45	0.87	0.41	0.78
0.50	0.89	0.49	0.80
0.55	0.90	0.55	0.82
0.60	0.91	0.60	0.84

*from Bentz and Garboczi [20].

To quantify the amount of expansion we first consider the volume of concrete which can potentially undergo expansion. Let y_s be the volume fraction of the concrete which can participate in expansion due to sulfate reaction:

$$Y_s = f_c \, f_{C_3A} \qquad (8)$$

The factors f_c and f_{C_3A} and r are given by eqs. (5) and (6), respectively. If there is no C_3A, $f_{C_3A} = 0$ in eq. (8), and there will be no general expansion due to ettringite formation.

The net fractional increase in solid volume on reaction, X_p, is given by:

$$X_p = b \, r \, y_s \, v \, \alpha_r / (1-\epsilon) \qquad (9)$$

Since expansive products do not form in gel pores, as the amount of capillary pore space decreases, $r \rightarrow 0$ and $X_p \rightarrow 0$.

In eq. (9) ϵ is the porosity of the product phase. For example, considering ettringite, ϵ would be the fraction voids between the ettringite crystals. The degree of reaction, α_r ranges from zero (no reaction) to unity (complete reaction). The reactant ratio, b, is defined as the total volume of solid reactant to the volume of the rate limiting solid reactant. The rate limiting reactant is the one which is completely consumed when reaction goes to completion ($\alpha_r = 1$). For reactions involving C_3A, the C_3A itself is the rate limiting reactant. This would include, e.g.,

reactions (B) and (D) of Table 2. The parameter b is unity when there is only one solid reactant, as, for example, with the calcium hydroxide of reaction (C). As with parameter v, b depends only on the reaction stoichiometry and is independent of the extent of reaction. It can be calculated from a knowledge of phase densities and reaction stoichiometry. To illustrate, consider reaction (B) of Table 2. The rate limiting reactant will be C_3A assuming that gypsum can be continuously produced via reaction (C). Thus, for reaction (B):

$$b = \frac{volume\ C_3A + volume\ C\bar{S}H_2}{volume\ C_3A} = [1 + 3\rho_{M,C_3A}/\rho_{M,C\bar{S}H_2}] = 3.5 \quad (10)$$

Values of the molar densities are given in Table 1. The values of parameter b for this and other reactions are summarized in Table 2.

The predicted fractional expansion (X) is given by:

$$X = h\ (X_p - \phi_c), \quad X_p > \phi_c$$
$$X = 0, \quad X_p \le \phi_c \quad \textbf{(11)}$$

Here, ϕ_c is the capillary porosity of the concrete. The constant h is introduced to account for the degree to which the potential expansive volume, as measured by $(X_p - \phi_c)$, is translated into actual expansion. If h=1 all of the expansive products would cause expansion, while for h<1 only some of the potentially expansive products would create expansion. The lower the value of h the less efficient is this process. Note that h<1 is most likely since reaction products can fill not only the pore space but also additional space created by cracking.

Atkinson and Hearne [6] observed in experimental studies that only about 1/20 of the ettringite formed is caused expansion, which indicates that h~0.05. This implies that ettringite can form and grow in cracks as well as in pores.

4. RESULTS AND DISCUSSION

Eq. (11) is a mathematical model which predicts the fractional expansion X of cementitious materials exposed to sulfate solutions. It is presumed that capillary pores will be able to accommodate stresses until they are filled with expansive products so that no general expansion will occur so long as $X_p \le \phi_c$. The criterion for expansion is $X_p > \phi_c$. However, some expansion may occur even if pores are not filled with reaction products, if crystals of the reaction products grow across the

10

capillary pores rather than uniformly filling the pore volume. In general a reaction product which forms closely to where the solid reactants dissolve is more likely to exert expansive stresses than one which forms remotely [17]. Thus ettringite is more likely to have a higher value of h than gypsum. Also, ettringite is more likely to have a higher value of h than gypsum since it can exert higher local expansive stresses [5, 13].

By solving eq. (11) at the point where expansion potentially begins ($X_p = \phi_c$):

$$\alpha_{rc} = \phi_c(1 - \epsilon)/bry_s v \qquad (12)$$

α_{rc} is the degree of reaction at which the capillary pores are calculated to be filled. If the α_{rc} calculated from (12) is greater than unity then the capillary pores can fully accommodate the increased net solid volume resulting from the reaction and no expansion is predicted. This occurs when X = 0 in eq. (11).

The capillary porosity ϕ_c is a function of w/c and the degree of hydration (α) of the cement [16, 22]:

$$\phi_c = f_c \frac{(w/c) - 0.39\alpha}{(w/c) + 0.32}, \ for \ (w/c) > 0.39\alpha \qquad (13)$$

Equation (13) is valid for (w/c) > 0.39α. At or below w/c = 0.39α there will be no capillary pores so that:

$$\phi_c = 0, \ for \ w/c \leq 0.39\alpha \qquad (14)$$

Sample calculations of maximum fractional expansion, $(Xp)_{max}$, and capillary porosity ϕ_c were performed using eqs. (9), (11), and (13) for both reactions (A) and (B) of Table 2 at two different values of w/c: 0.35 and 0.45. $(Xp)_{max}$ is the value of X_p when all of the rate limiting reactant is consumed ($\alpha_r = 1$). For reaction (A) the rate limiting reactant is monosulfate, while for reaction (B) it is tricalcium aluminate. Two different degrees of hydration were used; α_f and $\alpha_f/2$. The results of the calculations are presented in Table 4. The results show that the conversion of monosulfate and gypsum to ettringite (reaction (A)) is not predicted to be expansive regardless of the w/c level in the range studies, the degree of hydration, or the C_3A content. This is because $X_p < \phi_c$ in all cases studied. It is worth noting, however, that the reaction could still be locally expansive if ettringite crystals grow in the same place previously occupied by reacting monosulfate crystals. The volume expansion model only predicts the overall or macroscopic likelihood of expansion and does not account for possible

expansion on a local or microscopic level.

In contrast the conversion of C_3A and gypsum to ettringite (reaction (B)) is potentially expansive at some C_3A level between 2.75 and 11.1%. This is because the ϕ_c values in Table 4 lie between the calculated values of $(X_p)_{max}$.

Equation (12) was used to calculate the degree of reaction α_{rc} (as conversion of C_3A) at which the ettringite first becomes potentially expansive. The calculated values of α_{rc} for reaction (B) are presented in the last column of Table 4. For example, for a concrete made with a cement containing 11.1% C_3A with (w/c) = 0.35 and which is 40 percent hydrated, the capillary pores are predicted to become full of ettringite when 30% of the C3A present has reacted to form ettringite.

For reaction (B) one can also calculate, using eqs. (6), (8) and (9), the weight fraction C_3A (W_{C_3A}) at which the concrete becomes expansive. Together these equations predict that $(X_p)_{max} \propto (W_{C3A})_{max}$, where $(W_{C3A})_{min}$ is the minimum weight fraction of C_3A sufficient to permit expansion. For any value less than this, the model predicts that there will be no expansion since $(X_p)_{max} < \phi_c$. Model calculations show that at (w/c) = 0.35, $(W_{C_3A})_{min}$ is 2.8% at $\alpha_f = 0.8$ and 3.3% at $\alpha = 0.4$; whereas at (w/c) = 0.45, the corresponding values at $\alpha_f = 0.87$ and 0.44 for $(W_{C_3A})_{min}$ are 3.7% and 5%, respectively. These results predict that concrete made with cement having a lower water to solids ratio will undergo expansion via reaction (B) at lower C_3A contents than one made with a higher value of (w/c). Further, at lower ages, as shown by the results for $\alpha = \alpha_{f/2}$, there is more tolerance to C_3A content. Lower (w/c) concretes have fewer large capillary pores and lower capillary porosities (Table 4) and would appear to be more susceptible to sulfate attack. But low (w/c) concrete also has lower diffusivities [9] and a larger fraction of unhydrated C_3A may be occluded by hydration products. These factors may greatly reduce the access of sulfate ions to the C_3A in the concrete's interior and thus delay ettringite growth.

The reaction of sodium sulfate with calcium hydroxide to form gypsum (reaction (C)) was also investigated. For this reaction the expansion model must be modified somewhat since the rate limiting species will now be calcium hydroxide rather than C_3A. Because calcium hydroxide itself is a product of hydration its volume fraction f_{CH} will depend on the degree of hydration and the (w/c) ratio, and to a lesser extent on the cement composition. As shown by reactions (H) and (I), respectively, of Table 2, both C_3S and C_2S produce calcium hydroxide as a hydration product.

Table 4. Maximum Fractional Expansion $(X_p)_{max}$ and Capillary Porosity ϕ_c for Reactions (A) and (B) of Table 2.

Reaction	(w/c)	α	w_{C_3A}	$(X_p)_{max}$	$\phi_c, (\alpha_{rc})^*$
(A)	0.35	0.80[+]	2.75	0.18	1.0
			11.1	0.73	
		0.40	2.75	0.63	4.3
			11.1	2.5	
	0.45	0.87[+]	2.75	0.33	2.6
			11.1	1.3	
		0.435	2.75	0.66	6.5
			11.1	2.6	
(B)	0.35	0.80[+]	2.75	1.02	1.0
			11.1	4.1	(0.26)
		0.40	2.75	3.6	5.3
			11.1	14.3	(0.30)
	0.45	0.87[+]	2.75	1.9	2.6
			11.1	7.7	(0.33)
		0.435	2.75	3.6	6.5
			11.1	14.5	(0.45)

*values of α_{rc} calculated from eq. (12) are given in parentheses
+final expected degree of hydration [20].

Bentz and Garboczi [23] noted, however, that cement pastes, at least of ASTM Types I and II, produce pore and surface products which have similar volumes to those formed from C_3S paste. They also reported [20] that one volume unit of C_3S paste produces 0.61 units of calcium by hydroxide so that:

$$f_{CH} = \frac{0.61\,\alpha}{1 + 3.2\,(w/c)} \qquad (15)$$

For reaction (C), eq. (15) replaces eq. (6) of the expansion model, while the other equations of the model remain the same.

Table 5 presents sample calculations for reaction (6) made using the modified expansion model. The results show that since $(X_p)_{max} < \phi_c$ the formation of gypsum via reaction (C) is not expansive. An exception is noted for $(w/c) = 0.35$ at $\alpha = 0.80$ where $(X_p)_{max}$ and ϕ_c are of comparable magnitude. However, this degree of hydration is beyond the percolation threshold and sulfate ions provided by sodium sulfate would have difficulty in penetrating the concrete.

Table 5. Maximum Fractional Expansion $(X_p)_{max}$ and Capillary Porosity ϕ_c for Reaction (C) of Table 2.

w/c	α	f_{CH}, %	$(X_p)_{max}$, %	ϕ_c, %
0.35	0.80[+]	23.0	1.12	1.05
	0.40	11.5	1.96	4.28
0.45	0.87[+]	21.7	1.98	2.55
	0.435	10.9	1.87	6.46

[+]predicted degree of maximum hydration [20]

At lower degrees of hydration and higher values of (w/c) the pores are connected so that sulfate ions can more easily penetrate the concrete. However, in this case, the gypsum formed would be likely to be accommodated within the pore structure. Nevertheless, as with the formation of ettringite from monosulfate, some local expansion may occur so that in places the concrete may lose strength or have a lower modulus of elasticity. Thus, it has been observed that mortar bars kept in concentrated

solutions of Na_2SO_4 under conditions of controlled pH, where gypsum formation is likely, lose strength and expansion occurs [24].

5. SUMMARY AND CONCLUSIONS

A model has been developed which predicts both the conditions under which volumetric expansion of cementitious materials is most likely and the amount of expansion expected. The model is based on the concept of excluded volume, whereby, the amount of expansion is presumed to be proportional to the difference between the net solid volume and the original capillary porosity. Model parameters include concrete composition, phase densities, (w/c) ratio, degree of hydration, extent of reaction, and reaction stoichiometry.

The model was applied to three different reactions: the conversion of monosulfate and gypsum to ettringite; the conversion of C_3A and gypsum to ettringite; and the conversion of calcium hydroxide to gypsum. The model predicted that ettringite formation from monosulfate would not cause expansion. However, local expansion could occur if ettringite occupied the same space vacated by reacting monosulfate. The model predicted that if sufficient unhydrated tricalcium aluminate (C_3A) was available in mature cement paste and it reacted with gypsum to form ettringite, the reaction could cause expansion at low w/c ratios. Also, it was predicted that no expansion would result from the conversion of calcium hydroxide to gypsum.

6. ACKNOWLEDGEMENTS

7. REFERENCES

1.   .R. Clifton and L.I. Knab, "Service Life of Concrete," ~STIR 89-4086, National Institute of Standards and ~hnology (1989).

2.   de for Durable Concrete," ACI 201.2R-77, ACI Manual of .ete P. .tice, Part 1-Materials and General Properties of ..rete, . .erican Concrete Institute (1992).

3. ...F. Young and W. Hansen, "Volume Ratios for C-S-H Formation

Based on Hydration Stoichiometries," in Microstructural Development during Hydration of Cement, eds. L.J. Struble and P.W. Brown, Material Research Society Symposium Proceedings, Vol. 85, pp. 313-322 (1986).

4. J. Pommersheim and J. Chang, "Kinetics of Hydration of Tricalcium Aluminate in the Presence of Gypsum," Cement and Concrete Research, Vol. 18, pp. 911-922 (1982).

5. P.K. Metha, Concrete Structure, Properties and Materials, Prentice-Hall Inc. (Englewood, NJ, 1986).

6. A. Atkinson and J. Hearne, "Mechanistic Model for the Durability of Concrete Barriers Exposed to Sulfate-Bearing Groundwaters," Materials Research Society Proceeding 176, pp. 149-156 (1990).

7. F.M. Lea, The Chemistry of Cement and Concrete, Chemical Publishing Company, Inc. (New York, 1971).

8. J.R. Clifton, D.P Bentz, and J.M. Pommersheim, "Sulfate Diffusion in Concrete," NISTIR, National Institute of Standards and Technology (in press).

9. R.F. Feldman, J.J. Beaudoin, and K.E. Philipose, "Durable Concrete for a Waste Repository - Measurement of Ionic Ingress," Materials Research Society Symposium Proceedings, Vol. 176, pp.129-142 (1990).

10. E. Winkler, Stone: Properties, Durability in Man's Environment, 2nd ed., Springer-Verlag (New York, 1975).

11. P.K. Metha and F. Hu, "Further Evidence for Expansion of Ettringite by Water Absorption," Journal of American Ceramic Society, Vol. 61, pp. 179-181 (March-April, 1978).

12. P.K. Metha, "Mechanism of Sulfate Attack of Portland Cement Concrete-Another Look," Cement and Concrete Research, Vol. 13, pp. 401-406 (1983).

13. M. Deng and M. Tang, "Formation and Expansion of ettringite Crystals," Cement and Concrete Research, Vol. 24, pp. 119-126 (1994).

14. P.K. Metha, Cement and Concrete Research, Vol. 3, pp 1 (1973).

15. P.K. Metha and O.E. Gjørv, "A New Test for Sulfate Resistance of Cements," Journal of Testing and Evaluation, Vol. 2 (6), pp. 510-514 (1974).

16. M. Geiker, "A Study of Portland Cement Hydation," Ph.

Dissertation, Institute of Mineral Industry, Technical
University of Denmark (1983).

17. I. Odler and I. Jawed, "Expansive Reaction in Concrete," in
Material Science of Concrete, pp. 105-130, American Ceramic
Society (1991).

18. E.M. Gartner and J.M Gaidis,"Hydration Mechanisms, I," in
Material Science of Concrete, ed. J. Skalny, pp. 95-125,
American Ceramic Society (1989).

19. D.P. Bentz, P.E. Stutzman, and E.J. Garboczi, "Experimental
and Simulation Studies of the Interfacial Zone in Concrete,"
Cement and Concrete Research, Vol. 22, pp. 891-902 (1992).

20. D.P. Bentz and E.J. Garboczi, "Modelling Leaching of Calcium
Hydroxide from Cement Paste: Effects on Pore Space
Percolation and Diffusivity," Materials and Structures, Vo.
25, pp. 523-533 (1992).

21. J.M. Pommersheim and J.R. Clifton, "Models of Transport
Processes in Concrete," NISTIR 4405, National Institute of
Standards and Technology (1990).

22. L.O. Högland, "Some Notes on Ettringite Formation in
Cementitious Materials: Influence of Hydration and
Thermodynamic Constraints for Durability," Cement and
Concrete Research, Vol. 22, pp. 217-228 (1992).

23. D.P. Bentz and E.J. Garboczi, "Percolation of Phases in a
Three-Dimensional Cement Paste Microstructural Model," Cement
and Concrete Research, Vol. 21, pp. 325-344 (1991).

24. P. Brown, "An Evaluation of the Sulfate Resistance of Cements
in a Controlled Environment," Cement and Concrete Research,
Vol. 11, pp 719-727 (1981).

8. NOMENCLATURE

b	reactant ratio, eq. (10).
f_c	volume fraction of cement in concrete, eq. (5).
f_{CH}	volume fraction of $Ca(OH)_2$ in cement, eq. (15).
f_{C3A}	volume fraction of C_3A in cement, eq. (6).
h	proportionality constant for expansion, eq. (11).
r	volume fraction of capillarity pores, eq. (7).
$r_{1/2}$	value of r at $\alpha_f/2$.
r_f	value of r at αf.
v	volumetric expansion factor, eq. (1).
w_{C3A}	mass fraction of C_3A in cement.
$(w_{C3A})_{min}$	minimum value of w_{C3A} which can cause expansion.
w/c	water-to-cement ratio by mass.
y_s	volume fraction of concrete participating in expansion, eq. (8)
α_f	final degree of hydration.
α_r	degree of hydration.
α	degree of hydration which fills capillary pores, eq. (12).
ϵ	porosity within ettringite product phase.
ϕ	capillary porosity, eq. (13).
ρ_a	density of air.
ρ_c	density of cement.
ρ_{C3A}	density of C_3A.
ρ_s	density of aggregate.
ρ_w	density of water.
ρ_M	molar density.
$\rho_{M,C3A}$	molar density of C_3A.
$\rho_{M,C\bar{S}H_2}$	molar density of gypsum.

*Volume units which react relative to one volume unit of C_3A

C_3A

$+$

2.5^* $CaSO_4 \cdot 2\,H_2O$

$+$

$Ca(OH)_2$ 1.1^*

5.3^* H_2O

$\Rightarrow$

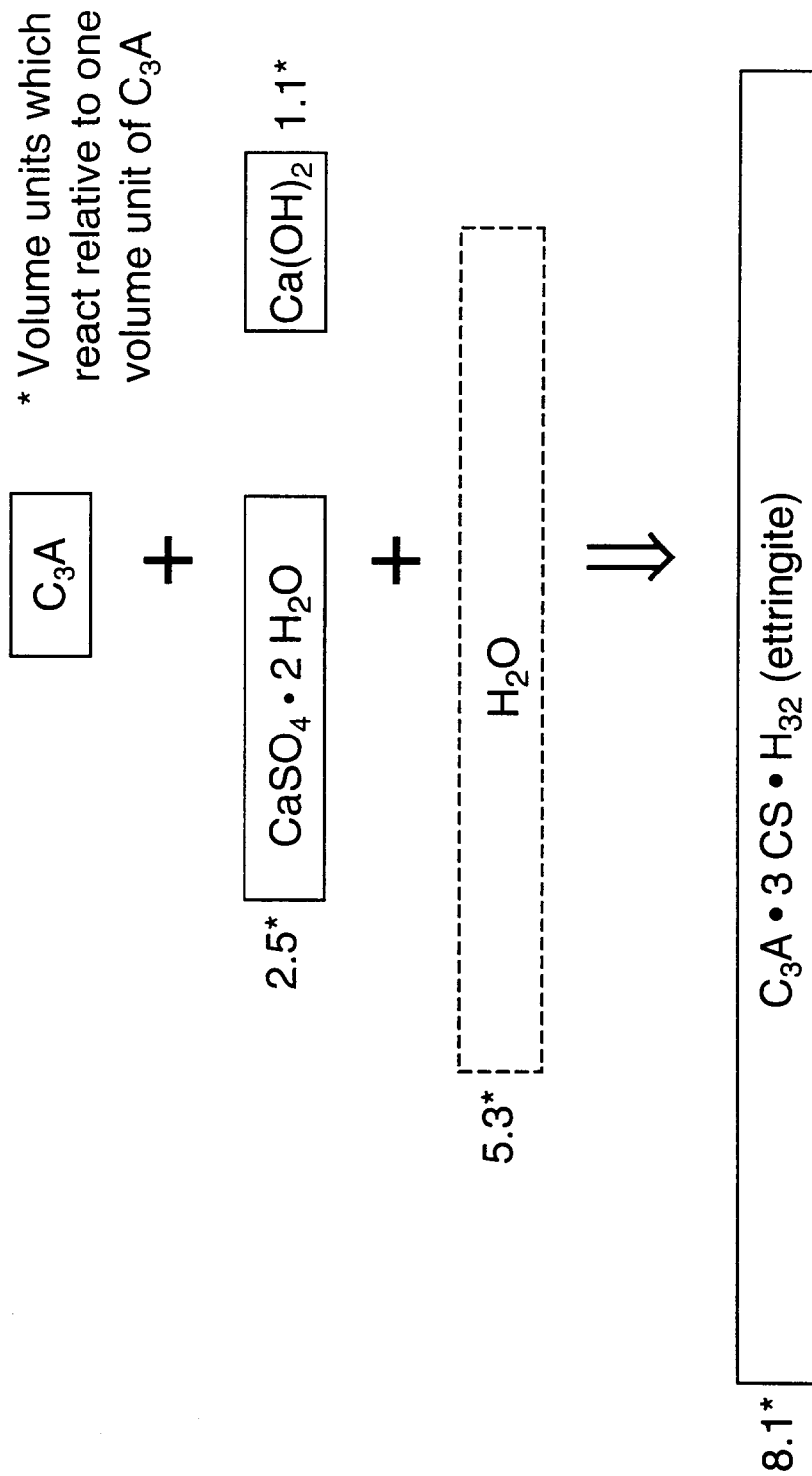8.1^* $C_3A \cdot 3\,CS \cdot H_{32}$ (ettringite)

Figure 1. Volumetric Relations in Ettringite Formation: Reactions (B) and (C) of Table 2.