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Communication

Changes in the size of pores during shrinkage (or expansion) of cement paste and concrete

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Abstract

The often-argued and seldom-resolved issue of relating the bulk shrinkage of concrete to changes in the size of pores is analyzed using a simple model. It is shown that the pores in a composite containing both shrinking and nonshrinking solid phases can themselves either shrink or expand when the matrix shrinks, depending on the amount of restraint in the system. The analysis also applies to expansive deformations, which occur with some types of chemical attack of cement paste. A mathematical relationship between the degree of restraint in a composite and the relationship between bulk volume changes and pore volume changes is given. These observations provide guidelines for interpreting the meaning of gaps that often form between aggregate and paste in concrete.

Keywords: Drying; Expansion; Shrinkage; Modeling

1. Introduction

When concrete is examined under a microscope, gaps are often observed between the paste and the aggregate particles. The presence of a gap is intuitive evidence that the volume of paste has changed since set. Surprisingly, it is not obvious whether gaps are caused by expansion or shrinkage of the paste. This issue has led to significant discussion at conferences, generally with no consensus reached, but has not been specifically addressed in the literature to our knowledge.

The expansion or shrinkage of cement paste can result from many physical phenomena. Moisture and temperature changes, sulfate exposure, freezing, and other exposure conditions can cause the paste to change dimensionally, and these changes have important effects on concrete performance, particularly deterioration. It is therefore important to understand why gaps can form, or indeed the circumstances leading to the expansion or contraction of any porosity.

In a two-phase system consisting of solid and pores, uniform expansion of the solid phase will clearly lead to enlargement of the pores, analogous to bread rising as it bakes. At the other extreme, if the same two-phase system is completely restrained so that the external dimensions cannot change, expansion of the solid phase must cause the pore volume to decrease. Concrete consists of solid phases that can shrink or expand (notably C-S-H), inert solid phases such as aggregate and CH, and pores. Additionally, phases such as ettringite and gypsum can precipitate in the smallest pores, causing swelling. While the total volume of concrete can and does change, the presence of inert solid phases ensures that there is some degree of restraint, so that neither of the above extreme cases holds. Thus, the effect of shrinkage or expansion of the C-S-H on the pore size will depend on the amount of restraint. A simple mathematical treatment of this problem is given here for consideration.

2. Discussion

2.1. Homogeneous volume change of a porous solid

Consider a sphere of radius R made up of a single solid phase. Now assume that the solid phase undergoes a homogeneous volume change:

$$V_\mathrm{f} = kV_\mathrm{i} \tag{1}$$

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where subscripts f and i designate initial and final states and k represents the ratio of the final volume to the initial volume. The sphere expands or shrinks uniformly, depending on whether k is greater or less than unity, so that the final radius is:

$$R_\mathrm{f} = \sqrt[3]{k}R_\mathrm{i} \tag{2}$$

Because the deformation is homogeneous, there are no stresses generated and the deformation of any particular location of the sphere is not affected by the deformation elsewhere. Now consider a porous solid represented in simplified form by the same sphere of solid phase but with a single pore of radius r located at its center. What is the change in the size of the pore when the solid phase undergoes a volume change k? Let V_i be the initial volume of solid phase. Then:

$$V_\mathrm{i} = 4/3\pi(R_\mathrm{i}^3 - r_\mathrm{i}^3) \tag{3}$$

and

$$V_\mathrm{f} = 4/3\pi(R_\mathrm{f}^3 - r_\mathrm{f}^3) = kV_\mathrm{i} \tag{4}$$

Combining Eqs. (3) and (4) gives:

$$(R_\mathrm{f}^3 - r_\mathrm{f}^3) = k(R_\mathrm{i}^3 - r_\mathrm{i}^3) \tag{5}$$

Because the deformation is homogeneous, the change in the outer radius of the sphere is unaffected by the presence of the pore at the center, and therefore Eq. (2) still holds. Combining Eqs. (2) and (5) gives:

$$(kR_\mathrm{i}^3 - r_\mathrm{f}^3) = k(R_\mathrm{i}^3 - r_\mathrm{i}^3) \tag{6}$$

and this reduces to:

$$r_\mathrm{f} = \sqrt[3]{k}r \tag{7}$$

Comparison of Eqs. (2) and (7) demonstrates that the pore will shrink or expand in the same way as the solid it replaced. Therefore, homogeneous expansion of the solid phase in a porous solid leads to larger pores, while homogenous shrinkage leads to smaller pores.

2.2. Homogeneous volume change in the presence of an inert phase

Consider a three-phase composite consisting of a deforming matrix phase, nondeforming inclusions, and pores. In this case, the inclusions are nonrestraining, meaning that their presence does not affect the ability of the matrix phase to deform. Let V_def be the initial volume of deforming phase, V_nondef be the volume of nondeforming phase, and V_p be the initial volume of pores. The initial volume of the composite is:

$$V_\mathrm{i} = V_\mathrm{def} + V_\mathrm{nondef} + V_\mathrm{p} \tag{8}$$

and after the matrix phase deforms the final volume is

$$V_\mathrm{f} = k_\mathrm{def}V_\mathrm{def} + V_\mathrm{nondef} + k_\mathrm{p}V_\mathrm{p} \tag{9}$$

where k_def and k_p are the ratios of the final to initial volumes of the deforming matrix phase and of the porosity, respectively. Dividing Eq. (9) through by V_i gives

$$k_\mathrm{tot} = k_\mathrm{def}X_\mathrm{def} + X_\mathrm{nondef} + k_\mathrm{p}X_\mathrm{p} \tag{10}$$

where k_tot is the ratio of final to initial volumes of the entire composite and X denotes the initial volume fraction of a phase. Because there is no restraint in this system, the pores will again deform in the same way as the total external dimensions of the composite (see Section 2.1), which means that

$$k_\mathrm{p} = k_\mathrm{tot} \tag{11}$$

Combining Eqs. (10) and (11) yields:

$$k_\mathrm{tot} = \frac{k_\mathrm{def}X_\mathrm{def} + X_\mathrm{nondef}}{(X_\mathrm{def} + X_\mathrm{nondef})} \tag{12}$$

Note that if is there is no inert solid phase ($X_\mathrm{nondef}=0$), then $k_\mathrm{tot}=k_\mathrm{def}$. From Eq. (12) it can be seen that

if $k_\mathrm{def} > 1$, then $1 < k_\mathrm{tot} < k_\mathrm{def}$

if $k_\mathrm{def} < 1$, then $k_\mathrm{def} < k_\mathrm{tot} < 1$

Thus, the volume change of the composite will be of the same sign but of a lesser magnitude than the volume change of the deforming phase due to the presence of the inert phase.

2.3. Fully restrained deformation

Consider the three-phase composite described above to be fully restrained so that its external dimensions cannot change. Now the initial and final volumes of the composite are the same and Eq. (8) can be set equal to Eq. (9):

$$k_\mathrm{def}V_\mathrm{def} + V_\mathrm{nondef} + k_\mathrm{p}V_\mathrm{p} = V_\mathrm{def} + V_\mathrm{nondef} + V_\mathrm{p} \tag{13}$$

Eq. (13) can be rearranged to give:

$$k_\mathrm{p} = 1 + \frac{V_\mathrm{def}(1 - k_\mathrm{def})}{V_\mathrm{p}} \tag{14}$$

Inspection of Eq. (14) indicates that if $k_\mathrm{def}>1$ then $k_\mathrm{p}<1$, and vice versa. Thus, under restrained conditions expansion of the solid phase will cause the pores to shrink, and shrinkage of the solid phase will cause the pores to grow.

2.4. Partially restrained deformation

The conditions of perfectly homogeneous deformation and completely restrained deformation represent extreme and rather unrealistic cases, analogous to the parallel and series models for computing material properties of a composite such as Young's modulus or thermal conductivity. Fig. 1 shows a two-dimensional composite consisting of a deforming phase sandwiched between two layers of non-deforming phase. This composite is fully restrained in the x-direction and unrestrained in the y-direction. In reality, most composites will deform under conditions of partial restraint. Because the effect of deformation of a solid phase on the pore size is different for unrestrained and fully restrained shrinkage, it may be readily envisioned that there exists a condition of partial restraint where the pore size will not change.

Deformation of a partially restrained three-phase composite is described by Eq. (10). In this case, the relationship between k_p and k_{def} will depend on both the degree of restraint in the composite and the volume fraction of the phases. At the ''critical'' degree of restraint such that there is no change in pore size, $k_p = 1$ and Eq. (10) reduces to:

$$k_{tot} = k_{def} X_{def} + X_{nondef} + X_p \tag{15}$$

Eq. (15) can be rearranged to give

$$k_{tot} = 1 + X_{def}(k_{def} - 1) \tag{16}$$

Eq. (16) represents the balance between the overall deformation of the composite and the deformation of the deforming phase such that the pore size does not change. This can be written as a fundamental inequality:

$$\begin{aligned} &\text{if } k_{tot} > 1 + X_{def}(k_{def} - 1), \text{ then pores grow} \\ &\text{if } k_{tot} < 1 + X_{def}(k_{def} - 1), \text{ then pores shrink} \end{aligned} \tag{17}$$

Note that the above relationships hold whether the deforming phase is expanding (k_{def}>1) or shrinking ($k_{def} < 1$).

It is useful to know how the pore volume ratio, k_p, varies with the deforming phase volume ratio, k_{def}, for a given amount of restraint. The degree of restraint in the system can be defined by the relationship between k_{tot} and k_{def}. As noted earlier, under conditions of complete restraint, $k_{tot} = 1$, i.e., there is no change in the bulk volume of the composite. Under unrestrained conditions, Eq. (12) holds. To generate a more general equation that bridges these two conditions, we introduce a new parameter R, the degree of restraint, which varies between 0 (no restraint) and 1(full restraint). The relationship between k_{tot} and k_{def} can be written as:

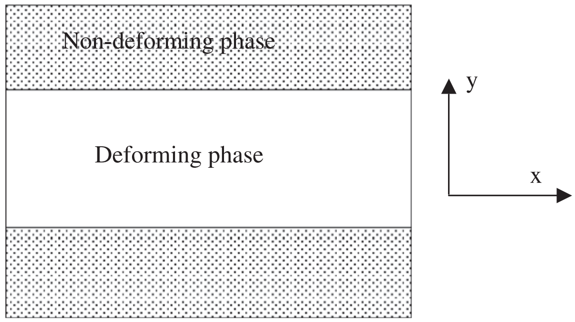

Fig. 1. Simple two-dimensional composite that is restrained in the x-direction (phases are in series) and unrestrained in the y-direction (phases are parallel).

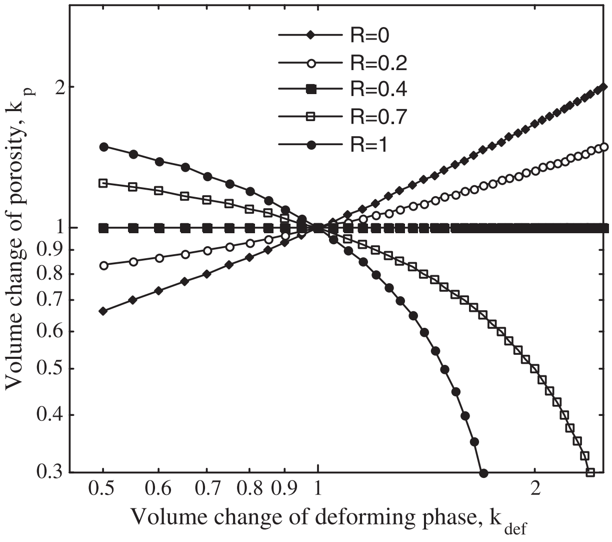

Fig. 2. Change in pore volume plotted against the volume change of the deforming phase. $R = 0$ indicates no restraint, and $R = 1$ indicates full restraint (no bulk volume change). Note that when $R = 0.4$ there is no change in pore volume.

$$k_{tot} = 1 + (1 - R)\left\{\left[\frac{k_{def} X_{def} + X_{nondef}}{(1 - X_p)}\right] - 1\right\} \tag{18}$$

When $R = 1$, Eq. (18) simply gives $k_{tot} = 1$, and when $R = 0$, Eq. (18) reduces to Eq. (12). The critical value of R resulting in no change in pore volume ($k_p = 1$) can be denoted R_c. An expression for R_c can be obtained by setting Eq. (16) equal to Eq. (18). This expression reduces to:

$$R_c = X_p \tag{19}$$

The critical level of restraint, R_c, is numerically equivalent to the initial volume fraction of porosity in the composite. Thus, the greater the porosity of the composite, the greater the level of restraint that must be applied to keep the pore size from changing during deformation of the solid phase. Note that it does not matter whether the restraint is applied externally or internally via the restraining effect of non-deforming inclusions.

Fig. 2 shows k_p plotted against k_{def} for various values of R, for a composite with $X_{def} = 0.4$, $X_{nondef} = 0.2$, and $X_p = 0.4$. In this case $R_c = X_p = 0.4$. For $R < R_c$, the pores expand when the deforming phase expands and shrink when the deforming phase shrinks. When R>R_c, the pores shrink when the deforming phase expands, and expand when the deforming phase shrinks.

2.5. Application to cement paste and concrete

When considering drying shrinkage, the deforming phase in cement paste at the length scale of microns can be considered to be a "cement gel" consisting of solid C-S-H, intermixed nanocrystalline CH, and the gel pores. All other solid phases are nondeforming, and the remainder of the volume is meso- and capillary porosity. For a mature, saturated paste with $w/c = 0.5$, the volume fractions can be approximated as $X_{\mathrm{def}} = 0.50$, $X_{\mathrm{nondef}} = 0.32$, and $X_{\mathrm{p}} = 0.18$ [1]. On drying, the bulk linear shrinkage will be about 1%, and thus $k_{\mathrm{tot}} = 0.97$.

Eq. (16) can be used to find the value of k_{def} for which the pore size does not change; for the above values, $k_{\mathrm{def}} = 0.94$. The volume change of the C-S-H gel on drying is certainly larger than 6% [2], and thus the capillary pores would be expected to expand on drying. In the extreme, this is why microcracks form on drying. That cement paste is a highly restrained composite on drying is also evident from its tendency to form larger shrinkage cracks.

Acknowledgements

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