

Constitutive Model for Predicting Ultimate Drying Shrinkage of Concrete

WILL HANSEN*

Department of Civil Engineering, The University of Michigan, Ann Arbor, Michigan 48109-2125

A constitutive model is derived from theory of elasticity for predicting ultimate drying shrinkage of concrete. The model was extended by incorporating the semiempirical composite model proposed by Hirsch and Dougill for predicting Young's modulus of concrete. Their composite model is the geometric mean of Paul's upper and lower limit boundaries of a two-phase composite. According to the shrinkage model the parameters needed for predicting ultimate drying shrinkage of concrete at any relative humidity of drying are the following: ultimate shrinkage of a paste of same water-to-cement (W/C) ratio and degree of hydration as the concrete, relative volume of aggregates and unhydrated cement, and the elastic properties of hydrated paste and the particles. The shrinkage model was tested on shrinkage results obtained in this study and by Pickett. Three different W/C ratios were covered together with a wide range in aggregate contents. Excellent agreement with the results was found.

I. Introduction

A NUMBER of factors control concrete shrinkage. These include relative humidity (rh),¹⁻⁴ aggregate content,^{2,5} W/C ratio,^{2,4,5} curing time,^{2,6} and admixtures.⁷⁻⁹

Current procedures recommended by ACI¹ for predicting concrete shrinkage are empirical. Since they are based on studies which covered a wide range of mix compositions, there is a lack of accuracy in predicting ultimate concrete shrinkage for a specific mix composition. Thus shrinkage may fall into the range of 415×10^{-6} to 1070×10^{-6} at 40% rh. Improvements in the accuracy of predicting drying shrinkage of concrete are desirable especially in prestressed concrete applications where drying shrinkage and creep significantly affect the long-term load-carrying capacity and deflection of a structure.

Constitutive models which represent an entirely different approach to predicting drying shrinkage have been proposed. Pickett⁵ developed a shrinkage model from theory of elasticity according to which drying shrinkage of concrete is determined from paste shrinkage and the volume concentration of aggregate. The shrinkage model developed by Hansen and Nielsen¹⁰ from theory of elasticity and composite theory includes a modulus ratio, defined as the ratio of Young's modulus of aggregate and cement paste in addition to paste shrinkage and aggregate content. However, modulus ratio has only a minor influence on concrete shrinkage within the range of values encountered in normal-weight concrete.

In the present study a shrinkage model for concrete is derived and tested on shrinkage results obtained in this study and on those reported by Pickett.⁵

II. Materials and Methods

A 0.4 W/C ratio mortar containing 50% Ottawa sand and graded according to ASTM C109 was cast in slabs and cured for 85 d at room temperature before being cut into thin specimens of approximately 2.3-mm thickness and 76-mm length.

Specimen fabrication, drying conditions, and shrinkage measurements are described in a previous study.¹¹

III. Concrete Shrinkage Model

(1) Derivation of Shrinkage Model

In a previous study¹¹ two stress-active shrinkage mechanisms were identified: (1) the surface free energy and (2) the capillary condensation effects. Both mechanisms predict that the hydration products will be under hydrostatic compression.

In concrete the hydrated paste constitutes a continuous matrix phase; shrinkage is reduced because of the presence of non-shrinking discrete particles (i.e., aggregate and unhydrated cement). Assuming linear elastic behavior the volumetric shrinkage $(\Delta v/v)_p$ of a fully hydrated paste is determined by

$$\left(\frac{\Delta v}{v}\right)_p = \frac{P_p}{K_p} \quad (1)$$

where P_p is the total hydrostatic shrinkage stress within the paste, and K_p is the bulk modulus of the paste. For concrete the shrinkage stress in the paste is reduced because of the restraint of aggregate and unhydrated cement. Thus the volumetric shrinkage of paste in concrete, $(\Delta v/v)_{pc}$, is given by

$$\left(\frac{\Delta v}{v}\right)_{pc} = \frac{P_{pc}}{K_p} \quad (2)$$

where

$$\left(\frac{\Delta v}{v}\right)_{pc} < \left(\frac{\Delta v}{v}\right)_p \quad (3)$$

Equation (2) can be rearranged since

$$v_{pc} = v_c - (v_a + v_{uc}) \quad (4)$$

where v_c is the volume of concrete, v_a is the volume of aggregate, and v_{uc} is the volume of unhydrated cement. Substituting Eq. (4) into Eq. (2) and dividing the left side by v_c in the numerator and the denominator yields

$$\frac{(\Delta v/v)_c}{1 - \frac{v_a + v_{uc}}{v_c}} = \frac{P_{pc}}{K_p} \quad (5)$$

where $(\Delta v/v)_c$ is the volumetric shrinkage of concrete. The relative restraining volume of dispersed particles is defined as

$$V_d = \frac{v_a + v_{uc}}{v_c} \quad (6)$$

where

$$0 \leq V_d \leq 1 \quad (7)$$

After substitution of Eq. (6) into Eq. (5) and rearrangement, it can be shown that

$$\left(\frac{\Delta v}{v}\right)_c = \frac{P_{pc}}{K_p} (1 - V_d) \quad (8)$$

From a composite point of view the same volumetric shrinkage of

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*Member, the American Ceramic Society.

concrete can be obtained by subjecting it to an external hydrostatic compressive stress P_c . Thus

$$\left(\frac{\Delta v}{v}\right)_c = \frac{P_c}{K_c} \quad (9)$$

where K_c is the bulk modulus of concrete. From Eqs. (8) and (9)

$$P_c = \frac{K_c}{K_p} P_{pc}(1 - V_d) \quad (10)$$

Further, the volumetric shrinkage of paste in concrete, $(\Delta v/v)_{pc}$, due to the paste shrinkage stress, P_{pc} , is equal to the volumetric paste shrinkage in a composite subjected to an external hydrostatic stress, P_p . Thus

$$\left(\frac{\Delta v}{v}\right)_{pc} = \frac{P_{pc}}{K_p} = \frac{P_p}{K_c} \quad (11)$$

Solving for P_{pc} in Eq. (11) and substituting this expression into Eq. (10) yields

$$P_c = P_p(1 - V_d) \quad (12)$$

In general

$$P = K \frac{\Delta v}{v} \quad (13)$$

For small strains

$$\frac{\Delta v}{v} = 3\varepsilon \quad (14)$$

where ε is the linear shrinkage strain. Using correct subscripts and substituting Eq. (14) into Eq. (13) and Eq. (13) into Eq. (12) it is found that

$$\frac{\varepsilon_c}{\varepsilon_p} = \frac{K_p}{K_c}(1 - V_d) \quad (15)$$

Equation (15) is not very useful in its present form since K_p and K_c are typically unknown. It can be modified from composite theory and microstructural considerations.

For a homogeneous and isotropic two-phase composite, Paul's¹² upper and lower limit boundaries of the bulk modulus can be established from energy considerations. The lower limit is given by

$$K_{cl} = \left(\frac{1 - V_d}{K_p} + \frac{V_d}{K_d}\right)^{-1} \quad (16)$$

and the upper limit is given by

$$K_{cu} = (1 - V_d)K_p + V_dK_d \quad (17)$$

Typically for concrete it is assumed that Poisson's ratio of the two phases are equal. This would greatly simplify the two expressions since the bulk modulus of the two phases can be substituted directly with Young's modulus. However, for concrete or partially hydrated paste this is not reasonable since the Poisson's ratio of fully hydrated paste is 0.28¹³ and about 0.12 for high-quality particles.¹⁴ Since

$$K = \frac{E}{3(1 - 2\nu)} \quad (18)$$

where E and ν are Young's modulus and Poisson's ratio, respectively, Eqs. (16) and (17) can be rearranged to show that

$$E_{cl} = \frac{1 - 2\nu_c}{\frac{(1 - V_d)(1 - 2\nu_p)}{E_p} + \frac{V_d(1 - 2\nu_d)}{E_d}} \quad (19)$$

$$E_{cu} = \frac{1 - 2\nu_c}{1 - 2\nu_p} E_p(1 - V_d) + \frac{1 - 2\nu_c}{1 - 2\nu_d} E_d V_d \quad (20)$$

Hirsch¹⁵ and Dougill¹⁶ showed that concrete can be described by a semi-empirical equation which is the geometric mean of the

lower and upper bound equations (Eqs. (19) and (20)). For reasons of simplicity they ignored the effect of Poisson's ratio. Thus

$$\frac{1}{E_c} = 0.5 \left(\frac{1}{E_{cl}} + \frac{1}{E_{cu}} \right) \quad (21)$$

Using correct subscripts and substituting Eqs. (19) and (20) into Eq. (21), and Eqs. (21) and (18) into Eq. (15), one obtains the following equation:

$$\frac{\varepsilon_c}{\varepsilon_p} = 0.5(1 - V_d) \times \left[\frac{1}{1 - V_d + \frac{(1 - 2\nu_p)E_d V_d}{(1 - 2\nu_d)E_p}} + 1 - V_d + \frac{1 - 2\nu_d}{1 - 2\nu_p} \frac{E_p}{E_d} V_d \right] \quad (22)$$

It is convenient to define a modulus ratio as

$$m = E_d/E_p \quad (23)$$

and substitute k for $(1 - 2\nu_p)/(1 - 2\nu_d)$. Thus

$$\frac{\varepsilon_c}{\varepsilon_p} = 0.5(1 - V_d) \left[\frac{1}{1 - V_d + kmV_d} + 1 - V_d + \frac{1}{k} \frac{1}{m} V_d \right] \quad (24)$$

Equation (24) states that discrete nonshrinking particles embedded in a continuous matrix phase, which is shrinkage active, introduce a restraining effect. Total restraining effect depends on the volume concentration of these particles and the elastic properties of the two phases. This is in general agreement with findings by Pickett,⁵ and Hansen and Nielsen.¹⁰ Further, for normal-weight concrete in which the modulus ratio is >1 , a hyperbolic relationship between relative shrinkage, $\varepsilon_c/\varepsilon_p$, and relative restraining volume, V_d , is predicted according to Eq. (24). This is in good agreement with previous models^{5,10} and shrinkage results.^{5,10,17,18}

Figure 1 illustrates the effects of modulus ratio and aggregate content on relative shrinkage of concrete over that of fully hydrated paste. For reasons of simplicity the curves were estimated for concrete containing fully hydrated paste and aggregates with a Poisson's ratio of 0.12.

Equation (24) is then reduced to

$$\frac{\varepsilon_c}{\varepsilon_p} = 0.5(1 - V_d) \left[\frac{1}{1 - V_d + 0.58mV_d} + 1 - V_d + \frac{1.72}{m} V_d \right] \quad (25)$$

where V_d is the relative aggregate content by overall volume of concrete.

For normal-weight concrete the modulus ratio is typically in the range of 4 to 7. Within the range of concrete mix proportions (i.e., 60% to 80% aggregate by overall volume) a decrease of about 30% in drying shrinkage of concrete is predicted due to an increase in modulus ratio (m values) from 4 to 7. The shrinkage model by Hansen and Nielsen,¹⁰ which also includes the effect of modulus ratio on concrete shrinkage, predicts a decrease in concrete shrinkage of less than about 8% due to the same change in m values. The reason is that they used Paul's lower bound model for normal-weight concrete. Consequently within the range of aggregate contents found in concrete the aggregate has less effect on Young's modulus of concrete. Thus there is less effect from modulus ratio. This effect is entirely ignored in Pickett's modified equation according to which

$$\varepsilon_c = \varepsilon_p(1 - V_d)^{1.7} \quad (26)$$

According to this expression the shrinkage curve falls between the two predicted curves based on Eq. (25) for m values between 4 and 7. Clearly the proposed shrinkage model is more versatile than the modified model by Pickett since it includes a rationale for predicting effects of modulus ratio on concrete shrinkage. In the case where a fully hydrated paste and aggregate have the same Young's

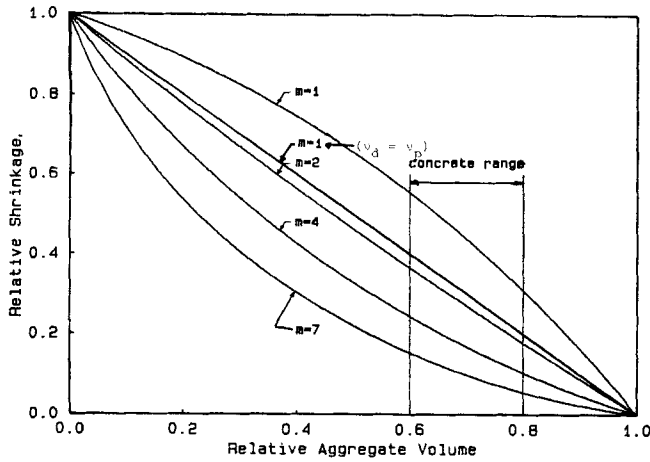


Fig. 1. Effect of modulus ratio on drying shrinkage of concrete.

modulus and Poisson's ratio, Eq. (24) is reduced to

$$\epsilon_c = \epsilon_p(1 - V_a) \tag{27}$$

which is in complete agreement with the expression derived by Hansen and Nielsen.¹⁰

(2) Application of the Proposed Shrinkage Equation on Concretes with Partially Hydrated Cement

In most cases concrete contains partially hydrated cement paste. Thus ϵ_p , which is the shrinkage of fully hydrated paste, is unknown. For these cases ultimate drying shrinkage of concrete is determined in two steps. First, the relative shrinkage ratio ϵ_c/ϵ_p of the partially hydrated paste of same W/C ratio and degree of hydration as the concrete is calculated using Eq. (24). However, the relative restraining volume of paste, $(V_d)_p$, is smaller than that of concrete. It typically ranges between 0 and 0.2. $(V_d)_p$ can be calculated using microstructural considerations.

For paste, the volume of unhydrated cement, v_{uc} , is determined by

$$v_{uc} = v_{co}(1 - \alpha) \tag{28}$$

where v_{co} is the volume of cement added originally and α is the relative degree of hydration, which varies between 0 and 1. Assuming constant volume of paste, v_p , during hydration

$$v_p = v_{co} + v_w \tag{29}$$

where v_w is the volume of water added to the cement. Also

$$v_w = \frac{W_w \delta_{ce} v_{co}}{\delta_w W_{co}} \tag{30}$$

where δ_w is the density of water and δ_{ce} is the density of unhydrated cement. W_{co} is the weight of cement, and W_w is the weight of water. The weight ratio, W_w/W_{co} , is the water-to-cement ratio (W/C). By substituting Eqs. (30) and (29) into Eq. (28) and using W/C instead of W_w/W_{co} , one can show that

$$(V_d)_p = \frac{v_{uc}}{v_p} = \frac{1 - \alpha}{1 + \frac{W}{C} \frac{\delta_{ce}}{\delta_w}} \tag{31}$$

For concrete the relative restraining volume is given by

$$(V_d)_c = \frac{1 - \alpha}{1 + \frac{W}{C} \frac{\delta_{ce}}{\delta_w}} (V_p) + V_a \tag{32}$$

where V_p is the relative paste content and V_a is the relative aggregate content. The only quantity in Eqs. (31) and (32) which is not readily known is α . It can be estimated with good accuracy in most cases from work by Taplin as cited in Soroka.¹⁹

Using Eqs. (31) and (24), $(\epsilon_c/\epsilon_p)_p$ is estimated in step 1 for partially hydrated paste. In step 2 the relative shrinkage ratio of concrete, $(\epsilon_c/\epsilon_p)_c$, is estimated by inserting $(V_d)_c$ from Eq. (32) into Eq. (25). Since $(V_d)_c$ is higher than $(V_d)_p$, a lower shrinkage ratio is obtained. Ultimate drying shrinkage of concrete is calculated from the two estimated shrinkage ratios and the measured shrinkage, ϵ_{pp} , of a partially hydrated paste using the following expression:

$$\epsilon_c = \epsilon_{pp} \frac{(\epsilon_c/\epsilon_p)_c}{(\epsilon_c/\epsilon_p)_p} \tag{33}$$

Table I. Prediction of Mortar Shrinkage at Different Aggregate Contents and W/C Ratios

V_a^*	$V_d^†$	Modulus ratio	Relative mortar shrinkage	Shrinkage ratio, Ottawa sand			Shrinkage ratio, Elgin sand		
				Predicted	Measured	Relative	Predicted	Measured	Relative
0.35 W/C ($\alpha = 0.65$) ¹⁹									
Type III cement									
0	0.167	4.29	0.709		0.370		0.370		
0.059	0.216	4.29	0.639	0.333	0.345	0.97			
0.061	0.217	4.29	0.636				0.332	0.338	0.98
0.173	0.311	4.29	0.516	0.269	0.272	0.99			
0.176	0.313	4.29	0.514				0.268	0.269	1.00
0.338	0.448	4.29	0.368	0.192	0.180	1.07			
0.520	0.599	4.29	0.234	0.122	0.094	1.30			
0.535	0.612	4.29	0.224				0.117	0.108	1.08
0.620	0.683	4.29	0.172				0.090	0.090	1.00
0.50 W/C ($\alpha = 0.73$) ¹⁹									
Type III cement									
0	0.105	6.76	0.755		0.587			0.587	
0.048	0.148	5.76	0.677				0.526	0.535	0.98
0.05	0.150	6.76	0.674	0.524	0.545	0.96			
0.15	0.239	6.76	0.537	0.417	0.450	0.93	0.417	0.372	1.12
0.30	0.373	6.76	0.376	0.293	0.285	1.03	0.293	0.270	1.09
0.50	0.552	6.76	0.218	0.169	0.170	1.00	0.169	0.165	1.02
0.67	0.705	6.76	0.118				0.092	0.089	1.03
0.4 W/C ($\alpha = 0.73$) ¹⁹									
Type I cement									
0	0.119	4.57	0.775		0.302				
0.50	0.560	4.57	0.258	0.100	0.112	0.89			

*Relative aggregate volume. †Relative restraining volume.

(3) Testing the Proposed Shrinkage Model

The shrinkage model derived in this study was used to predict ultimate drying shrinkage at 50% rh of three different W/C ratio mortars for which equilibrium paste and mortar shrinkage were obtained. The shrinkage of a 0.4 W/C paste was obtained in a previous investigation,¹¹ and the shrinkage of a 0.4 W/C ratio mortar containing 50% Ottawa sand was obtained in the present study. The equilibrium paste and mortar shrinkage of thin specimens (2.3 mm) dried at 50% rh is the shrinkage after 200 d of drying. This is reasonable, as shown in a previous study.¹¹ Shrinkage results for the two other paste and mortar systems were obtained by Pickett.⁵ The W/C ratios were 0.35 and 0.5, and the mortars had a wide range of aggregate contents. The aggregates used were Ottawa and Elgin sand.

Table I shows the calculated and measured mortar shrinkage values for the three W/C ratio systems, relative aggregate content, relative restraining volume, and ratio of predicted to measured shrinkage. Also shown are the measured paste shrinkage values.

For Ottawa and Elgin sand, Young's modulus is 75.9 GPa (11×10^6 psi),¹⁵ which is the same as that of unhydrated cement.²⁰ Young's modulus of the hydration products including micropores and capillary pores was estimated from the following equation obtained by Helmuth and Turk:¹³

$$E_p = E_s(1 - V_{cap})^3 \quad (34)$$

where E_s is Young's modulus of the hydration products including micropores. From experimental results a value of 31.5 GPa (4.55×10^6 psi) was estimated for E_s . V_{cap} is the relative capillary pore volume as a fraction of total paste volume. From microstructural considerations

$$V_{cap} = \frac{\frac{W}{C} - 0.36\alpha}{\frac{W}{C} + \frac{\delta_w}{\delta_{ce}}} \quad (35)$$

Using Eqs. (35), (34), and (23) a modulus ratio of 4.29, 4.59, and 6.76 was estimated for the 0.35, 0.4, and 0.5 W/C ratio systems of paste and mortar, respectively. These values were used throughout for each system and are shown in the third column of Table I.

The predicted shrinkage values are in excellent agreement with those measured except for one system (0.35 W/C mortar containing 52% Ottawa sand). The reasons for this deviation are not clear. Excluding this set the average ratio of predicted to measured values was found to be 101% based on 16 data sets, and nearly all the data were evenly distributed around the 100% value. The standard deviation between predicted and measured shrinkage was 0.06. This means that the predicted ultimate concrete shrinkage based on a 95% confidence interval is within 88% to 111% of the actual shrinkage. These results confirm the validity of the model and show that it can accurately predict mortar shrinkage. However, this can only be expected when the input parameters to the model such as ultimate paste shrinkage and aggregate modulus are known with good accuracy.

IV. Conclusions

- (1) A model was derived from the theory of elasticity for

predicting ultimate drying shrinkage of concrete. The usefulness of the model was greatly extended by including the semiempirical composite model for concrete derived by Hirsch¹⁵ and Dougill.¹⁶ The shrinkage model provides a rationale for incorporating the material parameters affecting ultimate concrete shrinkage at any given rh.

- (2) The hyperbolic shape of predicted relative concrete shrinkage vs aggregate content is in general agreement with previous proposed models by Pickett⁵ and Hansen and Nielsen²⁰ and shrinkage results. In the special case where the elastic properties of paste and aggregate are equal the proposed shrinkage model is identical with that of Hansen and Nielsen.¹⁰

- (3) The model was tested on shrinkage data obtained in this study and by Pickett for paste and mortar. Excellent agreement with shrinkage results was found.

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References

- ¹ACI Committee 209, "Prediction of Creep, Shrinkage and Temperature Effects of Concrete Structures," in SP-76: *Designing for Effects of Creep, Shrinkage, Temperature in Concrete Structures*. ACI, Detroit, MI, 1982.
- ²R. W. Carlson, "Drying Shrinkage of Concrete as Affected by Many Factors," *Proc., Am. Soc. Test Mater.*, **38** [2] 419-37 (1939).
- ³S. H. Kung and C. E. Kesler, "A Study of Free and Restrained Shrinkage of Mortar," T.A.M. Rept. No. 647, The Engineering Experiment Station, University of Illinois, 1964; 70 pp.
- ⁴S. E. Pihlajavaara, "A Review of Some of the Main Results of a Research on Aging Phenomena of Concrete. Effect of Moisture Conditions on Strength, Shrinkage and Creep of Mature Concrete," *Cem. Concr. Res.*, **4**, 761-71 (1974).
- ⁵G. Pickett, "Effect of Aggregate on Shrinkage of Concrete and a Hypothesis Concerning Shrinkage," *J. Am. Concr. Inst.*, **52** [5] 581-90 (1956).
- ⁶G. J. Verbeck and R. A. Helmuth, "Structure and Physical Properties of Cement Paste," *Proc. Int. Symp. Chem. Cem. 5th, Tokyo, 1968*, **3**, 1-32 (1969).
- ⁷R. F. Feldman and E. G. Swenson, "Volume Change on First Drying of Hydrated Portland Cement With and Without Admixtures," *Cem. Concr. Res.*, **5**, 25 (1975).
- ⁸R. L. Berger, J. H. Kung, and J. F. Young, "Influence of Calcium Chloride on Drying Shrinkage of Alite Paste," *J. Test. Eval.*, **4** [1] 85-93 (1976).
- ⁹G. M. Bruere, S. D. Newbegin, and L. M. Wilson, "A Laboratory Investigation of the Drying Shrinkage of Concrete Containing Various Types of Chemical Admixtures," Div. Miner, C.S.I.R.O., Technical Paper No. 1, Melbourne, Australia, 1971.
- ¹⁰T. C. Hansen and K. E. C. Nielsen, "Influence of Aggregate Properties on Concrete Shrinkage," *J. Am. Concr. Inst.*, **62** [7] 783-94 (1965).
- ¹¹W. Hansen, "Drying Shrinkage Mechanisms in Portland Cement Paste": this issue, preceding article.
- ¹²B. Paul, "Prediction of Elastic Constants of Multiphase Materials," *Trans. Metall. Soc. AIME*, **218** [1] 36-41 (1960).
- ¹³R. A. Helmuth and D. H. Turk, "Elastic Moduli of Hardened Portland Cement and Tricalcium Silicate Pastes: Effect of Porosity," *Highw. Res. Board, Spec. Rep.*, **90**, 135-44 (1966).
- ¹⁴M. Anson and E. Newman, "The Effect of Mix Proportions and Method of Testing on Poisson's Ratio for Mortars and Concretes," *Mag. Concr. Res.*, **18** [56] 115-29 (1966).
- ¹⁵T. J. Hirsch, "Modulus of Elasticity of Concrete as Affected by Elastic Moduli of Cement Paste Matrix and Aggregate," *J. Am. Concr. Inst.*, **59** [3] 427-51 (1962).
- ¹⁶J. W. Dougill, "Discussion of Paper by T. J. Hirsch [Ref. 15]," *J. Am. Concr. Inst.*, **59** [9] 1363-65 (1962).
- ¹⁷O. Ishai, "Influence of Sand Concentration on Deformation of Mortar Beams Under Low Stresses," *J. Am. Concr. Inst.*, **58** [5] 611-23 (1961).
- ¹⁸D. W. Hobbs, "The Dependence of the Bulk Modulus, Young's Modulus, Shrinkage and Thermal Expansion of Concrete Upon Aggregate Volume Concentration," Technical Rept TRA 437, Cement and Concrete Association, London, Dec. 1969; 16 pp.
- ¹⁹I. Soroka, *Portland Cement Paste and Concrete*; pp. 1-338, Macmillan Press Ltd., London, 1979.
- ²⁰C. E. Weir, C. M. Hunt, and R. L. Blaine, "Behavior of Cements and Related Materials Under Hydrostatic Pressures up to 10,000 Atmospheres," *J. Res. Natl. Bur. Stand. (U.S.)*, **56**, 39-50 (1956). □