Pergamon

Cement and Concrete Research, Vol. 25, No. 2, pp. 288-292, 1995

0008-8846/95 $9.50+.00

0008-8846(95)00011-9

CHEMICAL SHRINKAGE AND AUTOGENOUS SHRINKAGE OF HYDRATING CEMENT PASTE

Ei-ichi Tazawa*, Shingo Miyazawa* and Tetsurou Kasai**
* Department of Civil Engineering
Hiroshima University
Higashihiroshima, 724 Japan
** Department of Civil Engineering
Tokai University
Hiratsuka, 259-12 Japan

(Communicated by M. Daimon)
(Received October 13, 1994)

ABSTRACT

It is well known that the absolute volume of cement plus water decrease with progressive hydration. In this study, chemical shrinkage of cement was calculated from chemical equation of hydration, it was compared with observed one. Definition of chemical shrinkage and autogenous shrinkage was made and relationship between them was clearly described.

Foreword

A term frequently misused for autogenous shrinkage(1) is "hardening shrinkage". Since autogenous shrinkage is definitely different from hardening shrinkage, these terms should therefore be clearly defined at first. Hardening shrinkage is a term used for the phenomenon in which the volume of the hydrate produced by the reaction between unhydrated cement and water is smaller than the total volume of the cement and water. It is also called "chemical shrinkage". Autogenous shrinkage is a macroscopic reduction in length under constant temperature and without any moisture migration to or from the concrete.

Results and Discussions

Hardening shrinkage calculated from chemical equation(2,3)

The chemical reaction of portland cement is too complex to be shown by simple chemical equations. The chemical equations for each compound with coexisting gypsum at ordinary temperature are assumed as follows.

$$2C_2S + 6H_2O \longrightarrow C_3S_2H_3 + 3Ca(OH)_2 \quad (1)$$

$$2C_2S + 4H_2O \longrightarrow C_3S_2H_3 + Ca(OH)_2 \quad (2)$$

$$C_3A + 3(CaSO_4 2H_2O) + 26H_2O \longrightarrow C_3A3CaSO_4 32H_2O \qquad (3)$$
$$2C_3A + C_3A3CaSO_4 32H_2O + 4H_2O \longrightarrow 3[C_3ACaSO_4 12H_2O] \qquad (4)$$
$$C_3A + Ca(OH)_2 + 12H_2O \longrightarrow C_3ACa(OH)_2 12H_2O \qquad (5)$$
$$C_4AF + 3(CaSO_4 2H_2O) + 27H_2O \longrightarrow C_3(A{\cdot}F)3CaSO_4 32H_2O + Ca(OH)_2 \qquad (6)$$
$$2C_4AF + C_3(A{\cdot}F)3CaSO_4 32H_2O + 6H_2O \longrightarrow 3[C_3(A{\cdot}F)CaSO_4 12H_2O] + 2Ca(OH)_2 \qquad (7)$$
$$C_4AF + 10H_2O + 2Ca(OH)_2 \longrightarrow C_3AH_6\text{–}C_3FH_6 \text{ (solid solution)} \qquad (8)$$

At the earliest stage the reaction of C_3A will form ettringite as in equation (3), and at a later stage it will transform into monosulfoaluminate as in equation (4), and C_3A remaining from the shortage of gypsum will follow equation (5). The absolute volume of all compounds are decreased after reaction as is understood from each equation. An example of the shrinkage calculated for equation (1) is as follows.

	$2C_2S$	$+ 6H_2O$	$\longrightarrow C_3S_2H_3$	$+ 3Ca(OH)_2$
Weight	456.6	108.1	342.5	222.3
Specific gravity	3.15	1.0	2.71	2.24
Volume	145.0	108.1	126.4	99.2
	253.1		225.6	

$$\text{Chemical Shrinkage} \qquad \frac{(253.1 - 225.6)}{253.6} \times 100 = 10.87\ (\%)$$

Densities of each compounds used in the calculation were adopted form references (4) and (5). The degree of hydration at each reaction time were adopted from the data by G.Yamaguchi et al. at early stage of hydration, and from those by Copeland et al. for later age after one day. As a result, the total shrinkage of cement paste at each reaction time was obtained from the sum of the shrinkage of each compound obtained from the mineral composition, the shrinkage ratio and the degree of hydration of each compound. The volume change of gypsum was neglected in the calculation.

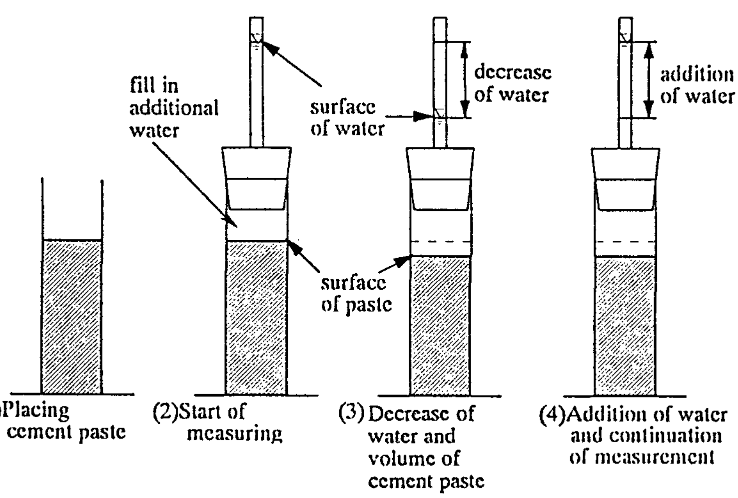


FIG.1
Measuring chemical shrinkage of cement paste

Method of measuring chemical shrinkage

As explained in the Foreword above, chemical shrinkage is not measurable by length change or the rubber bag method by Le Chatelier (see the following Chapter). As shown in Fig.1, cement paste is placed in a container and water is immediately added on top of the paste. And then volume change is measured with a measuring pipette mounted on the top of the water. It should be noted that the exterior water may not fully permeate into internal voids when they are being formed, depending on the water–cement ratio and the depth of the paste. It is advantageous to ensure a large interface on shallow cement paste. For cement paste with low water–cement ratio, 300 ml Ehlenmeyer flasks, in which pastes were placed at depths of 3–12 mm depending on W/C, were used.

Chemical shrinkage was shown as the ratio of the volume reduction to the volume of cement paste before hydration. Observed chemical shrinkage is almost the same as the calculated value, as shown in Fig.2. It can be said that the assumptions in the chemical reaction of cement shown above are suitable.

Significance of the data obtained by Le Chatelier method

The Le Chatelier method is often referred in old books as a method of obtaining chemical shrinkage. This is a method in which only cement paste is contained and sealed in a rubber bag and volume change are determined by the weight change in water or according to the similar manner as described in the previous chapter. The values obtained by this method, however, have little technical significance.

The reasons are as follows: It is well known that, during bleeding testing, bleeding water is absorbed in the cement paste after a certain period. If water is further fed on the top surface, the water continues to be absorbed, proving that the level of bleeding water in set cement is lower than the top surface(6). The amount of the absorbed water corresponds to the chemical shrinkage after the point of time when the bleeding water disappears from the top surface, and is the volume change to be measured by the method previously mentioned. When the water transfer is interrupted by a rubber film, the chemical shrinkage is measured while the bleeding water exists

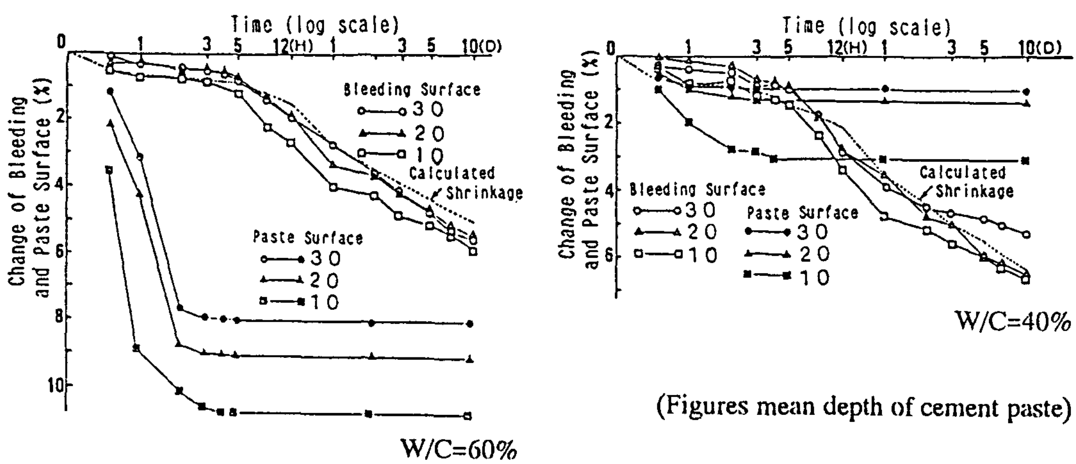


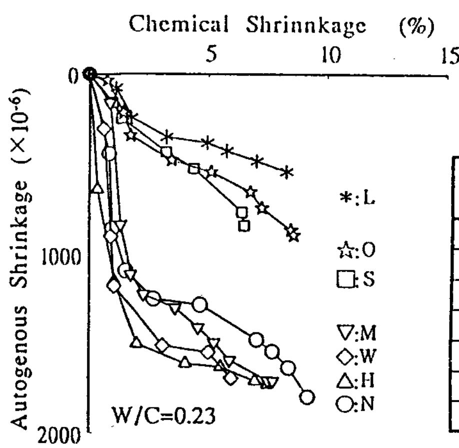
FIG.2
Relation between hydration time and change of bleeding and paste surface

on the top surface, but when the water level becomes lower than the cement surface, autogenous shrinkage thereafter is measured. The time when the level of bleeding water becomes lower than the top surface of cement normally does not coincide with the setting time. The Le Chatelier method therefore determines the total of the hardening shrinkage up to a very early age and the autogenous shrinkage after a certain point of time. In this sense, the data after a certain point of time is technically of little use, because chemical shrinkage at very early age is normally much larger than autogenous shrinkage (in the order of 10 to 100 times).

The purpose of measuring autogenous shrinkage is to grasp the macroscopic reduction in length after setting of cement in order to control cracking. The significance of the data is therefore jeopardized by the inclusion of chemical shrinkage. Also, data of chemical shrinkage becomes completely useless, e.g., for the prediction of internal voids in hardened cement, if chemical shrinkage is replaced with autogenous shrinkage after a certain age. Thus the data obtained by the Le Chatelier method is of little technical value.

Relation between chemical shrinkage and autogenous shrinkage

Chemical shrinkage is not at all related to the macroscopic volume change of cement or concrete, as shown in Fig.3. It is because the macroscopic volume change that occurs concurrently with chemical shrinkage can be either expansive or contractive. It is well known that the expansion of expansive cement is brought about by the formation of ettringite or calcium hydroxide, but either reaction is accompanied by chemical shrinkage. While chemical shrinkage can be predicted by simple stoichiometric calculations if the hydration equations are determined, and can be quantitatively verified by means of experiment. Also, this procedure readily explains the seemingly condraticting behavior of expansive cement. By this simple fact alone, it is easily understood that autogenous shrinkage is not proportional to chemical shrinkage, and that no simple relationship exists between them. Most of the chemical shrinkage turns into internal air voids within hardened cement paste(4), and autogenous shrinkage consists of very small part of chemical shrinkage as shown in Fig.4. But autogenous shrinkage is considerably large and comparable to drying shrinkage when it is expressed in terms of micro strain(8,9).



Type of cement	Mineral Compound (%)			
	C_3S	C_2S	C_3A	C_4AF
N	51.5	22.9	8.9	8.8
M	42.9	35.9	3.2	11.9
H	62.8	11.8	8.0	8.5
S	61.0	16.9	1.7	14.6
W	61.1	16.5	12.1	0.6
O	57.6	20.5	2.2	13.7
L	22.9	58.8	2.5	9.4

FIG.3
Relation between chemical shrinkage and autogenous shrinkage

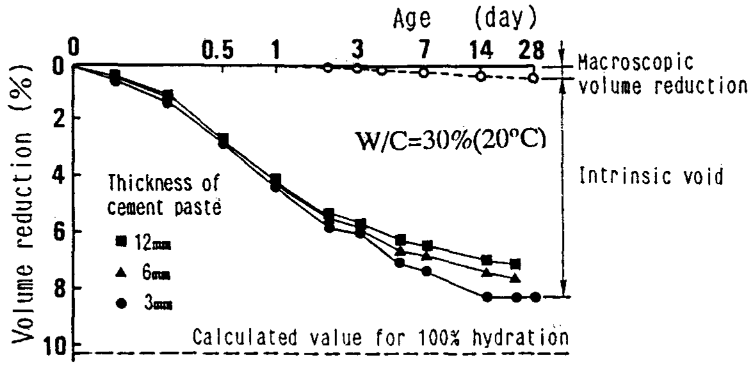


FIG.4
Chemical shrinkage and intrinsic void formation

Concluding Remarks

The observed value of chemical shrinkage coincided well with the theoretical value calculated from chemical equations. If the final chemical shrinkage at 100% hydration is precisely determined, it becomes possible to predict the degree of hydration of cement at a certain age by this proposed method. In order to measure chemical shrinkage correctly, it is important to adopt a proper experimental procedure with clear definition of chemical and autogenous shrinkages.

Acknowledgement

The author expresses his sincere gratitude to graduates and students of Structural Materials Laboratory of Hiroshima University who accomplished numerous experiments.

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