

INFLUENCE OF CURING TIME ON SHRINKAGE AND WEIGHT LOSS OF HYDRATING PORTLAND CEMENT

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Physical states of interstitial water of cement paste are differentiated by the measurement of two relationships; by the relationship between shrinkage and weight loss and by the relationship of shrinkage speed and weight loss speed with drying time. Curing time of the specimen is chosen as a main variable of the measurements. By analysing the former relationship, it is found that hydration process of cement can be treated by the reaction rate theory, and in the latter relationship four or five transition points are found. The transition points are interpreted phenomenologically and correlated with the shrinkage process and transformation of microstructure of cement paste with curing time.

1. INTRODUCTION

Cement paste can be regarded as a polyphase material even at its mature state, and many physical interactions can take place between phases, namely, gaseous, liquidus and solid phase. In almost all basic processes such as failure, deformation, deterioration, etc. certain kinds of interactions are observed whether a process is static or dynamic, elastic or inelastic, thermal or isothermal. No property of cement paste could be discussed completely, in this sense, as a phenomenon pertaining to only one phase.

Generally, the gaseous phase does not play a positive role on the behavior of cement paste except in the case of carbonation. Therefore, versatility in properties of cementitious material is mainly caused by the interaction between liquid and solid phase.

The contribution of this interaction to a particular property depends not only on the relative proportion of three phases but also on the internal structure. It is important to know transition of the internal structure with hydration process.

In this thesis, shrinkage weight loss relationship is chosen as one manifestation of the structural change. Curing time, specimen size and drying mode are adopted as main variables of the experiments. An analysis of shrinkage speed and weight loss speed is presented. Calculation of self-desiccation and dis-

ussion on hydration rate are written on the basis of the chemical equations proposed by Brunauer and Copeland.

2. LITERATURE

2-1 Literature on Shrinkage Weight Loss Relationship

Relationship between the movement of water and shrinkage has long been regarded as a cause-and-effect relationship. An elaborate review on this subject was made by Robert G. L'Hermite on Fourth International Symposium on Chemistry of Cement⁸⁾. He showed a schematic representation which suggests that the relationship between weight loss and shrinkage is linear for old specimens and curvilinear for young specimens. These two curves were drawn from origin probably because the length which was measured just before drying was assumed to be original. After referring to a few other experimental results, he concluded that there must be different forms of water in regard to shrinkage evaporation relation, that is

- a) a free water having little or no influence on the dimensional variations,
- b) a physically held water that is primarily involved in these variations, and
- c) a water more highly bonded in the structure that can be evaporated only under exceptional conditions of time or of temperature.

Verbeck's work¹⁰⁾, published in the same Symposium, suggested that two types of water are desorpted from cement paste, each type having a constant shrinkage/weight loss ratio over its operative range. Moreover, the two types of water had different heats of adsorption, yet each had a constant differential heat of adsorption over the entire range of water contents in which it operated.

R.F. Feldman and P.J. Sereda¹¹⁾ studied weight loss-dimensional change relationship for the purpose of differentiating between adsorbed and non-evaporable water. They hydrated the cement in a polyethylene bottle on a rotating wheel at water/cement

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ratio of 500% for 90 days. After the solution was dried over calcium chloride (11% R.H.), hydrated cement in powdered form was obtained. They compacted the sample under various loads which were varied from 5 000 lbs. to 65 000 lbs. for a disc shape mold 1.250 in. in diameter. Environmental conditions under which the compaction was made, were not referred to in this paper. A rectangular plate $1\frac{1}{8}'' \times 3\frac{3}{8}'' \times 1/16''$ was used for a specimen, which was placed in the vacuum, controlled in water vapour pressure. Measurements were made on each equilibrium state attained in this controlled water vapour pressure. By plotting dimensional change against weight loss, they discovered two linear portions in the curve connected by a break point and concluded that this point should be the datum point for zero adsorbed water. Also, the fact that a large proportion of the length changes occur in the low vapour pressure region was pointed out.

Harold Roper¹²⁾ indicated that it is possible to differentiate between various types of water lost by cement paste during drying. He used cement paste specimens having dimensions of $1/4'' \times 1/4'' \times 6''$ and water/cement ratios of 0.35 and 0.50. After 7 days curing in saturated air the bars were placed in controlled CO₂-free atmosphere having progressively lower relative vapour pressures. The bars were brought to equilibrium with the vapour pressure in each atmosphere before being measured and exposed to a drier condition. By plotting shrinkage against the corresponding weight loss, he obtained two curves which consisted of four sections of differing slopes, and each section was well represented by a straight line.

Also he measured heat of solution for a mature cement paste. By combining this result with shrinkage, he suggested that there is a constant relationship between the shrinkage and the heat of desorption except for some regions.

His third experiment was performed by means of sorption balance and extensometer which were specially designed for automatic measurement. The vapour pressure system was so controlled that water vapour was the only gas in contact with the specimen. Two specimens were cast using initial water/cement ratio of 0.33. One having dimension $1/4'' \times 1/8'' \times 5''$ was tested after 28 days of curing and another $1/4'' \times 1/4'' \times 5''$ specimen was tested after 180 days in a similar manner to the first experiment. Relative vapour pressure was varied from 1.0 to 0.05. He found four or five inflection points of relative vapour pressure in both of its relations with shrinkage and weight loss. These results, however, were not consistent enough with the results from the first experiment.

2-2 Structural Models Proposed for Explanation of Shrinkage Process

Driving force of drying shrinkage has long been ascribed to the capillary tension expressed by the Kelvin equation.

$$F = \sigma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) = - \frac{RT}{MV_f} \ln \frac{P}{P_s}$$

where

r = principle radii of water surface curvature,

σ = surface tension of water,

V_f = specific volume of water,

M = molecular weight of water,

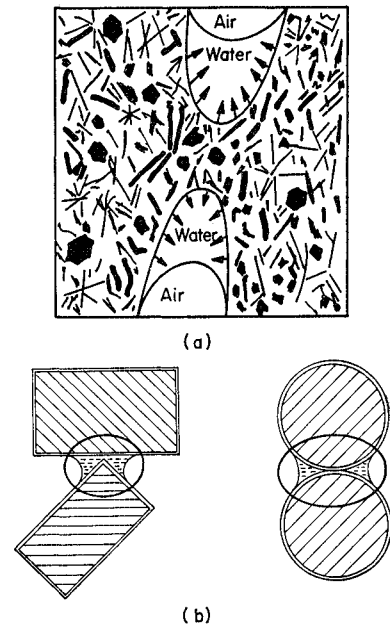
R = gas constant,

T = absolute temperature,

P_s = vapour pressure over plane surface at temperature T , the saturated vapour pressure, and

P = the existing vapour pressure over a concave surface.

T.C. Powers¹³⁾ proposed a capillary condensation theory as a mechanism of shrinkage using this equation. However, the structural models suggested by him (Figure 1-b) may not be considered to be realistic enough because such models give rise to rather small elastic strain in local part of cement hydrate or grain. If we assume a stepwise meniscus as is shown in Figure 1-a, hydrostatic tension set up in larger pores can be distributed in smaller size pores, and mechanism of deformation resembles seepage creep. As evaporation proceeds from the



T. C. Power's Model of Capillary Condensation

Fig. 1 Structural Models for Explanation of Shrinkage Process.

larger size pores, some amount of water can flow out from the small pores and shrinkage strain can be distributed uniformly.

3. DISCUSSION ON SHRINKAGE DUE TO CHEMICAL REACTION OF CEMENT

As is commonly observed for a chemical reaction, hydration of cement accompanies volume change as an inevitable consequence. Absolute volume of hydration products is less than the total volume of reactants. Unless water is supplied from outside, this difference in volume is compensated mainly by increase in microvoids and slightly by macroscopic decrease in paste volume. This phenomenon is often referred to as "self-desiccation".

As the hydration process is recognized as a crystallization process in nature, this kind of volume change may not have great influence on residual stress problem except in a few secondary interactions.

The volume change can only occur at crystall-solution interface or at clinker-solution interface and since the hydration takes place with a solution step, the volume change can be compensated by subsequent movement of water.

One of the secondary effects may be caused by this movement of water which is possibly responsible for redistribution of hydration nuclei and hence some change in solidification speed.

Solidification does not take place into air-filled space built up by "self-desiccation", and this might explain the reasons why water-curing is necessary for development of strength of concrete or why a completely sealed specimen does not exhibit strength as high as that of water-cured concrete. Therefore, it is important to know the magnitude of volume change of this origin.

A set of equations which was published by Brunauer and Copeland¹⁴⁾ was adopted to calculate an approximate value of the volume change.

A)	$2(3 \text{ CaO} \cdot \text{SiO}_2) + 6 \text{ H}_2\text{O} = 3 \text{ CaO} \cdot 2 \text{ SiO}_2 + 3 \text{ H}_2\text{O} + 3 \text{ Ca}(\text{OH})_2$			
weight (g)	456.8	108.0	342.5	222.3
density	3.15	1	2.85	2.23
absolute volume (cc)	145.0	108.0	120.2	99.7
	253.0		219.9	
	Volume shrinkage = $\frac{253.0 - 219.9}{253.0} = 13.1\%$			
B)	$2(2 \text{ CaO} \cdot \text{SiO}_2) + 4 \text{ H}_2\text{O} = 3 \text{ CaO} \cdot 2 \text{ SiO}_2 + 3 \text{ H}_2\text{O} + \text{Ca}(\text{OH})_2$			
weight (g)	344.6	72.0	342.5	74.1
density	3.28	1	2.85	2.23
absolute volume (cc)	105.1	72.0	120.2	33.1
	177.1		159.3	
	Volume shrinkage = $\frac{177.1 - 159.3}{177.1} = 10.6\%$			
C)	$4 \text{ CaOAl}_2\text{O}_3\text{Fe}_2\text{O}_3 + 10 \text{ H}_2\text{O} + 2 \text{ Ca}(\text{OH})_2 = 6 \text{ CaOAl}_2\text{O}_3\text{Fe}_2\text{O}_3 + 12 \text{ H}_2\text{O}$			
weight (g)	486.1	180.0	148.2	814.4
density	3.77	1.0	2.33	2.77
absolute value (cc)	129.0	180.0	66.5	294.0
	375.5		294.0	
	Volume shrinkage = $\frac{375.5 - 294.0}{375.5} = 21.7\% (4.86\%)$			
D)	$3 \text{ CaOAl}_2\text{O}_3 + 12 \text{ H}_2\text{O} + \text{Ca}(\text{OH})_2 = 3 \text{ CaOAl}_2\text{O}_3\text{Ca}(\text{OH})_2 + 12 \text{ H}_2\text{O}$			
weight (g)	270.3	216.0	74.1	560.4
density	3.04	1.0	2.23	2.15
absolute volume (cc)	88.9	216.0	33.2	260.2
	338.1		260.2	
	Volume shrinkage = $\frac{338.1 - 260.2}{338.1} = 23.0\% (14.6\%)$			
E)	$3 \text{ CaOAl}_2\text{O}_3 + 10 \text{ H}_2\text{O} + \text{CaSO}_4 \cdot 2 \text{ H}_2\text{O} = 3 \text{ CaOAl}_2\text{O}_3\text{CaSO}_4 + 12 \text{ H}_2\text{O}$			
weight (g)	270.3	180.0	172.0	622.5
density	3.04	1.0	2.50	1.95
absolute volume (cc)	88.9	180.0	68.9	319.0
	347.8		319.0	
	Volume shrinkage = $\frac{347.8 - 319.0}{347.8} = 8.28\%$			

The above calculation is not correct for reactions C) and D), because calcium hydroxide in these equa-

tions is produced by reactions A) and B). Figures in parenthesis were obtained by neglecting this by-product.

Densities of C₃S, β-C₂S and tobermorite were adopted from a paper by Brunauer and Greenberg¹⁵⁾, and all others from the "Chemistry of Cement and Concrete" by Lea & Desch¹⁶⁾.

If the complete hydration is assumed in these equations, the maximum shrinkage (S_c)_{max} of a cement paste mixed into its theoretical W/C due to the chemical reaction, can be written as

$$(S_c)_{max} = \frac{17 M_a + 11 M_b + 81 M_c + 78 M_d - 59 M_e}{1.27 M_a + 0.89 M_b + 3.09 M_c + 3.05 M_d + 0.33 M_e} \dots\dots\dots(1)$$

where

- M_a = specific moles of C₃S per gram of cement,
- M_b = specific moles of C₂S per gram of cement,
- M_c = specific moles of C₄AF per gram of cement,
- M_d = specific moles of C₃A per gram of cement,
- M_e = specific moles of CaSO₄·2 H₂O per gram of cement.

In this calculation, volume change due to hydration of gypsum was neglected and specific moles of gypsum were so modified as to include hydrated water. As a matter of course, the equation (1) will indicate sensitivity to "self-desiccation" of a particular cement.

If the degree of hydration is assumed for each reaction, the equation (1) can be generalized as a function of curing time in more complicated form. Only the results obtained for the cement used in this experiment are shown in Figure 2. Even for a water cement ratio that is encountered in practice, 8 to 10% of shrinkage in terms of paste volume was predicted. A part of this shrinkage may also be compensated by setting shown in Figure 3, as well

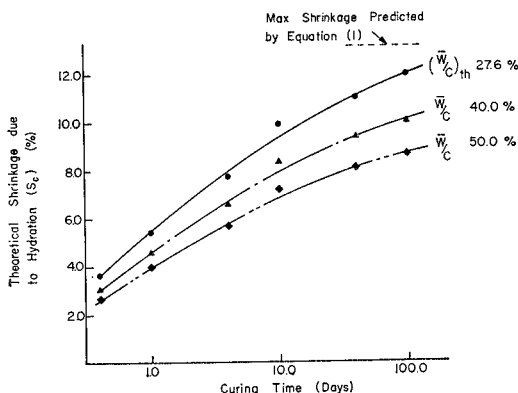


Fig. 2 Shrinkage due to Chemical Reaction as a Function of Curing Time.

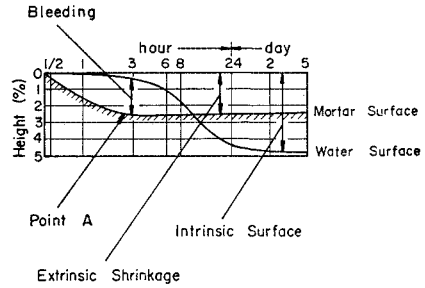


Fig. 3 Extrinsic Shrinkage and Intrinsic Shrinkage.

as by macroscopic shrinkage discussed before. But it is expected that substantial amount of void can be created in a completely sealed specimen.

4. OBJECT OF STUDY AND METHOD OF ATTACK

4.1 Object of Study

Electron microscope has been extensively used to study microstructure of hardened cement paste, and much of the information obtained by this technique has increased our understanding of various properties of cementitious material. Techniques of replica preparation have been greatly improved, while compositions of specimen have been varied extensively. It is certain that electron microscopy is and will be one of the most promising and powerful methods to study microstructure of cement paste, and that much effort will be concentrated on it in the future.

But this does not mean that the electron microscope is the only way to study microstructure. Many properties of cement paste are sensitive to its moisture content. This is partly due to the volume change associated with moisture change and sometimes due to the difference in contribution of the liquid or gaseous phase to the particular property. Research in this area is difficult to carry out under electron microscope, because a dry sample has to be used to make a replica or a thin film for transmission. Even if a wet specimen can be prepared, it was impossible to observe it as it is under electron microscope due to the vacuum system involved. There is some possibility a method could be devised to make a one stage replica of a wet sample, but this has not been successful to date. Pre-shadowing is not available for a wet sample for the same reasons. And it is much more difficult to observe structural change caused by moisture movement using one specimen. This difficulty in direct observation may be a main reason why mechanism of shrinkage of cement paste is not well understood yet.

As the volume of evaporable water remains essentially constant regardless of the bonding force with solid surface, it is reduced to the weight of water

which could be measured macroscopically. If we could differentiate the weight of water by some technique, the volume of water dispersed in structure of cement paste could be differentiated, which might be helpful in understanding the effect of moisture content mentioned before. The object of this study lies in trying this analysis through macroscopic measurement on shrinkage and weight loss.

Shrinkage up to 1% in length may or may not influence the basic internal structure of cement paste, but it should be noted that the volume of evaporable water is much greater than the macroscopic decrease in volume corresponding to that amount of weight loss, and presumably this relationship depends on curing time, in other words, degree of hydration. We can easily imagine such a model that satisfies the above condition and subjects great influence on internal structure by drying. By analysing the relationship between shrinkage and weight loss, the suitability of such a model can be checked. This is useful not only to deduce mechanism of shrinkage but also to enable better interpretation of electron micrographs.

As is shown in section 2-1, almost all of the research on shrinkage weight loss relationship has been conducted adopting fairly long curing time, and none of them have varied the degree of hydration of cement paste. Since complete evaporation of capillary water might essentially stop further hydration, in other words, might stop solidification of cement paste into void space, shrinkage weight loss relationship and hence location of break points shown in the previous discussion (section 2-1) will change under various curing conditions. Experimental determination of the break points under various curing conditions and their mutual interaction with specimen size and drying condition might provide some information on curing process or hydration process as well as on shrinkage process.

Series 1 to 3 were conducted in open air without avoiding contamination by CO_2 . Many other studies on this subject avoided carbonation by eliminating CO_2 from air. As far as the engineering problems are concerned, drying shrinkage does not occur without accompanying subsequent carbonation. One reason why the contamination was avoided in so many projects is that this process was considered to be a problem at surface or near surface portion of a specimen, but drying shrinkage and carbonation are both processes that proceed from surface and their effect on overall strain could be accumulated over whole range of time as the inelastic and non-equilibrated shrinkage process proceeds. Therefore contamination might be as important as drying shrinkage.

In series 3, specimens are kept in a desiccator

except during measurement. Substantial amount of contamination could be avoided by this method, though not all of it. By comparing these two sets of measurement, effect of contamination can be discussed.

Shrinkage process is neither a uniformly dispersed process nor a stationary process in nature. The magnitude of deformation is dependent upon history of environment and may be not independent of inelasticity of cement hydrate. Therefore, shrinkage is sensitive to the path through which a system reaches to an equilibrium state, and one equilibrium states does not correspond to one invariant state in an environment. This is why measurements were taken along a non-stationary path to an equilibrium state under constant environmental conditions rather than on each equilibrium state under various environmental conditions. And this is also the reason why specimen size was varied. The main purpose of this study is to try an analysis of a non-stationary shrinkage process with reference to time as a variable.

4-2 Method of Measurement

Length of specimen prepared into different cross-section was measured according to the method prescribed in ASTM C 490-65 T. At the same time the specimen was weighed on a balance recording the time of measurement. Accuracy of the dial gage used was ± 0.0001 in. and that of the balance was ± 0.05 gram.

The following items were kept in mind throughout the measurement.

- 1) Metallic tips which were buried in a specimen to fit the measuring device should keep same contacts at every measurement later on.
- 2) Weight measurements were made as quickly as possible, also taking care that reading was taken while the balance was moving.
- 3) Dial gage was checked at every measurement using metallic standard. This reading varied 0.0002 in. throughout all measurement, which was negligibly small compared to variation in length of a specimen.
- 4) All of the specimens were wiped by a piece of cloth soaked with acetone to get form grease out of surface.
- 5) Each specimen was placed on two horizontal beams which supported a specimen at one third of its length from both ends. Enough space was secured between specimen laid at right angle on the two beams. (series 1, 2 and 5)

4-3 Preparation of a Specimen

All of specimens were prepared using same W/C ratio and same materials except for those specimens tested in series 5. Type 1 cement was used (Her-

cules brand). Mixing water was kept at room temperature. Properties of cement are shown in Table 1.

Cement was mixed according to the prescription of ASTM C 305-65. The value of W/C adopted was 45% except in series 5 where it was impossible to control W/C . This value was selected rather arbitrarily taking mixing, placing, compaction and bleeding into consideration. But this value should be corrected for absorption of moisture from air during initial curing in moist room.

A relation between cement and water surface in a form is expressed by Figure 3 schematically. Osker Völter¹⁷⁾ tried to define extrinsic shrinkage and intrinsic shrinkage using this figure (here the word shrinkage used in "extrinsic shrinkage" is identical with setting).

Considering this figure, cement paste was cast 1/4 in. thicker than the top level of a form. When the situation indicated by the point A in Figure 3 has

Table 1

Properties of Cement used in the Experiment	
Type and Specification:	Hercules, Type I
Chemical:	
Silica (SiO_2)	20.12%
Alumina (Al_2O_3)	5.81%
Ferric Oxide (Fe_2O_3)	2.53%
Lime (CaO).....	62.96%
Magnesia (MgO)	3.80%
Sulfur Trioxide (SO_3).....	
when $3\text{CaOAl}_2\text{O}_3$ is 8% or less	
when $3\text{CaOAl}_2\text{O}_3$ is more than 8%.....	
Ignition Loss	2.48%
Insoluble Residue	0.99%
Potential Compounds	
Tricalcium Silicate (3CaOSiO_2)	54.00%
Tricalcium Aluminate ($3\text{CaOAl}_2\text{O}_3$)	11.20%
Tricalcium Silicate & Tricalcium Aluminate.....	
Dicalcium Silicate	16.80%
Tetracalcium Alumino Ferrite	7.60%
CaSO_4	4.30%
Physical:	
Fineness, Specific Surface, Wagner.....	1793
Air Permeability, Blaine.....	3209
Soundness, Autoclave Expansion	0.320%
Time of Setting, Gillmore	
Initial (Hr. : Min.)	3 : 20
Final (Hr. : Min.).....	5 : 30
Tensile Strength, psi	
1-Day	
3-Day	
7-Day	
Compressive Strength, psi	
1-Day	1633
3-Day	3158
7-Day	4158
.....	5508
Air Entrainment, % by Volume	9.8%

been obtained (about 2 hours from placing) the top of the specimen was cut and the surface was finished. Then net weight of the cement paste which was cast in a form was weighed. The form was placed in a moist room of constant temperature (70°F) until it was stripped after 24 hours.

By the time of stripping, the cement paste gained weight of 1.1% in average. Therefore actual W/C was 46.6%.

Initial reading was taken after 24 hours from mixing except for those specimens which were cured less than 24 hours. Then all specimens were cured in water at room temperature. Curing time represents the time from mixing to the end of the curing in water. Total length of a specimen was 6.2 in. and effective gage length was 4.875 in. For saturated specimens that were cured in water, weight was measured after wiping their surface carefully with a piece of dry cloth.

4-4 Factors Varied

Five series of experiments were conducted. Curing time, drying mode and specimen size were main factors varied.

Series 1 : $1'' \times 1''$ cross section was used. Curing time was varied into 6 hours, 23 hours, 4 days, 9 days, 22 days and 122 days. Specimens were kept in constant humidity room (46 to 52% R.H. and $70 \pm 1^\circ\text{F}$ from actual record). Three specimens were measured for each condition.

Series 2 : $1'' \times 5/8''$ and $1'' \times 3/8''$ cross sections were used. Curing time was varied into 10 hours, 1 day, 7 day, and 18 days. Test condition was same as that of series 1.

Series 3 : Specimens were kept in a desiccator which contains magnesium perchlorate. The desiccator was kept in a constant temperature room ($70 \pm 1^\circ\text{F}$). Curing time and specimen size tested were same as series 2.

5. DISCUSSION AND ANALYSIS OF DATA

5-1 Effect of Curing Time on Shrinkage and Weight Loss

Figures 4 through 8 were obtained by plotting shrinkage against weight loss in terms of cement paste weight. Figures 4 through 8 represent the results from series 1, series 2, and series 3, respectively. All of the figures show that curing time has great influence on both shrinkage and weight loss.

From practical point of view, it is interesting to note that the maximum shrinkage did not occur either in well-cured or poorly-cured cement paste

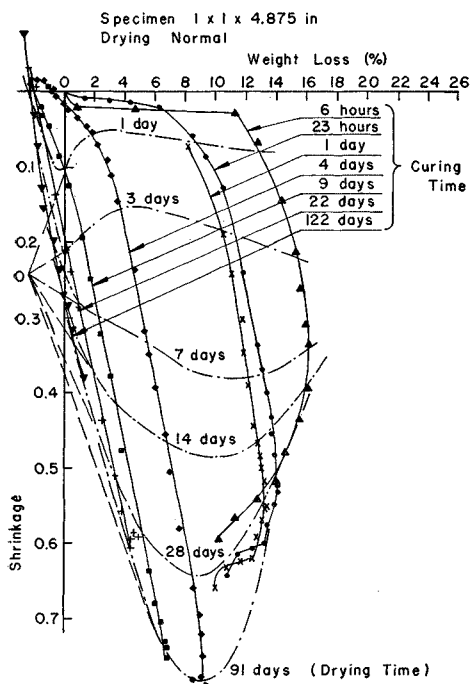


Fig. 4 Shrinkage Weight Loss Relationship (Normal Drying) 1' x 1' x 4.875' Specimen.

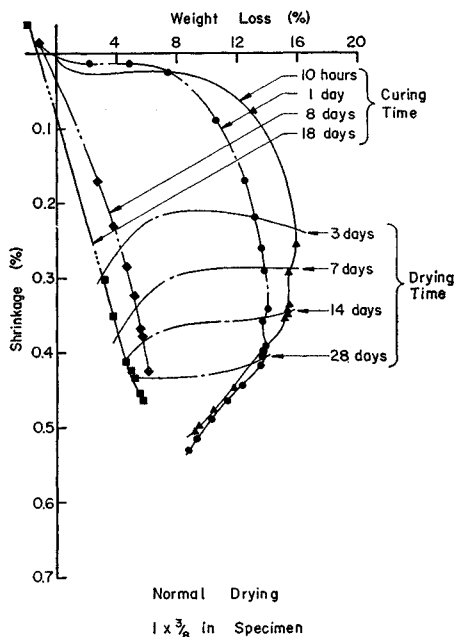


Fig. 6 Shrinkage Weight Loss Relationship (Normal Drying) 1' x 3/8' x 4.875' Specimen.

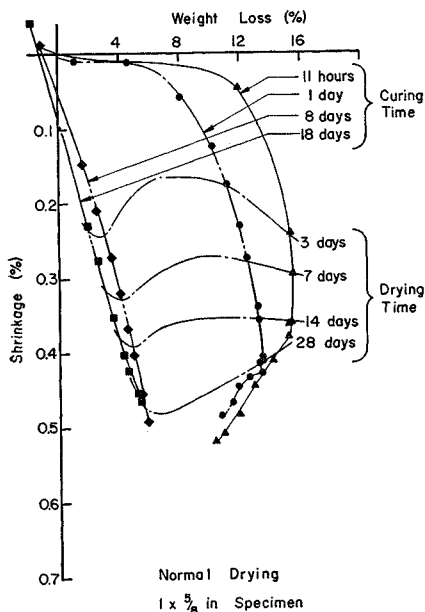


Fig. 5 Shrinkage Weight Loss Relationship (Normal Drying) 1' x 5/8' x 4.875' Specimen.

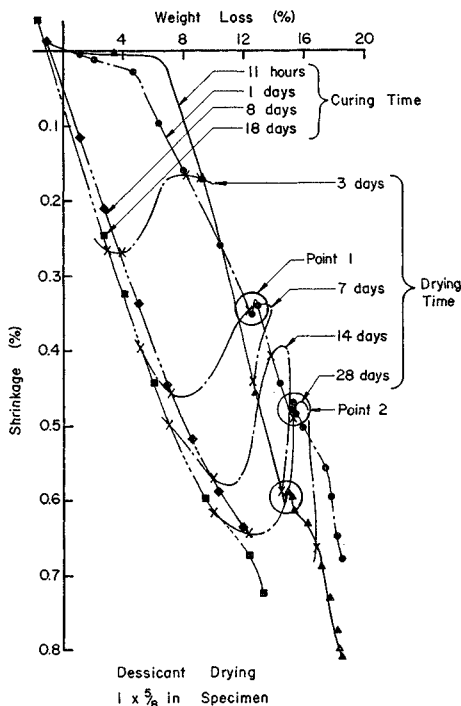


Fig. 7 Shrinkage Weight Loss Relationship (Desiccant Drying, Magnesium Perchlorate) 1' x 5/8' x 4.875' Specimen.

(Figure 4). The maximum shrinkage was observed for specimens cured for 4 days, this value was twice as much compared to the value obtained for specimens cured for 122 days. This fact seemingly contradicts the experience that more cracking tends to occur in well cured concrete. For smaller size specimens, this effect becomes less prominent (Fig-

ures 5, 6). None of the curves showed sharp break point; some linear part, however, was observed in each curve towards later age of drying. Slopes of this linear part in Figure 4 were essen-

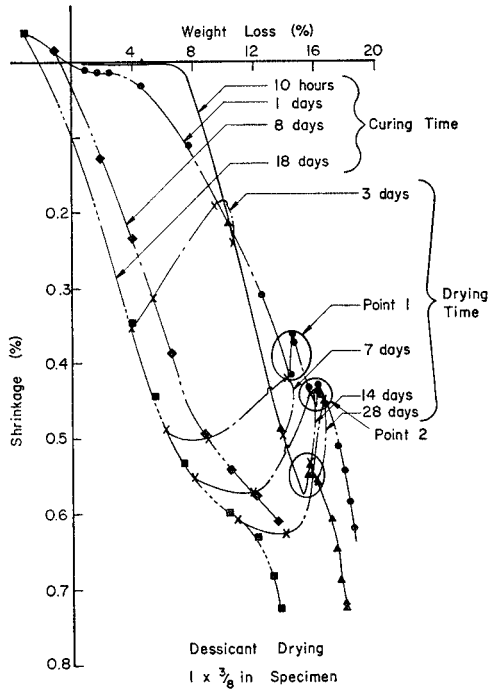


Fig. 8 Shrinkage Weight Loss Relationship (Desiccant Drying, Magnesium Perchlorate)

tially same for each curing time, which possibly suggests that no significant change has occurred in contacts between cement grains due to prolonged curing. The distance between these lines may be equivalent to the weight of water which has been combined either chemically or physically during corresponding curing time.

5-2 Discussion on Hydration Process

The amounts of combined water were deduced either by extrapolating these lines or by using a technique described in section 5-3 for poorly-cured specimens, while the theoretical values of hydrated water were calculated from chemical equations shown in section 3. The degree of hydration which was suggested by Copeland and Kantro¹⁸⁾ was introduced in this calculation.

The rates of hydration (W/C) calculated from the above two sets of data were plotted against curing time (t_c) using a logarithmic scale. Approximately, two linear relations were obtained for each case as is shown in Figure 9. The rate of hydration in this figure was expressed in terms of grams of combined water per 100 grams of original cement per day. By least square method, these lines can be written as

$$(W/C)_m = 7.135 t_c^{-1.475} \text{ (measured)} \dots\dots (2)$$

$$(W/C)_c = 4.305 t_c^{-1.166} \text{ (calculated)} \dots\dots (3)$$

which are basically the same type of equations as will be predicted from reaction rate theory. Ver-

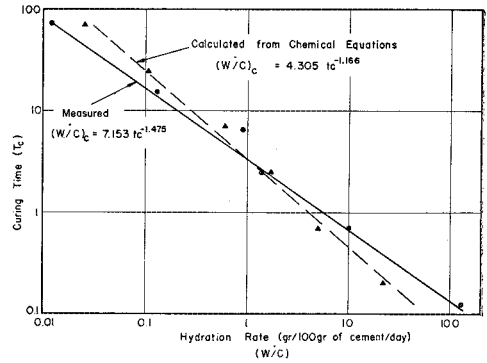


Fig. 9 Hydration Rate vs. Curing Time.

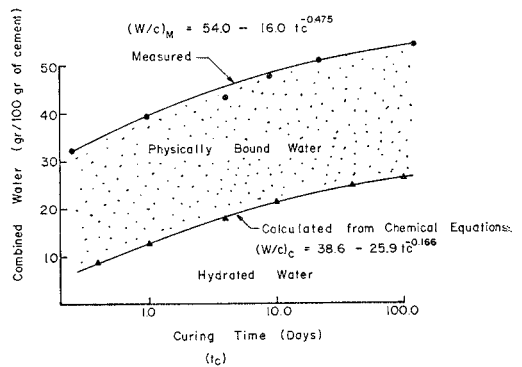


Fig. 10 Combined Water vs. Curing Time.

beck¹⁹⁾ showed that the relation between the rate of hydration and curing temperature can be discussed in terms of reaction rate theory. By combining this with the result shown above, we could argue that hydration process could be treated by reaction rate theory. As a natural consequence of this result, curing time under water from mixing can be identified with reaction time.

The equations (2) and (3) were integrated and the integral constants were so determined as to fit the data within that range of time.

$$(W/C)_m = 54.0 - 16.0 t_c^{-0.475} \text{ (measured)} \dots\dots\dots (4)$$

$$(W/C)_c = 38.6 - 25.9 t_c^{-0.166} \text{ (calculated)} \dots\dots\dots (5)$$

The difference between these two curves is considered to be physically bound water as is shown in Figure 10. The amount of physically bound water does not increase much by continuous curing after setting of cement paste, and can be written as

$$(W/C)_{ph} = 15.4 - 16.0 t_c^{-0.475} + 25.9 t_c^{-0.166} \dots\dots\dots (6)$$

The ratio between the equation (6) and the equation (4) could be an indication of degree of inelasticity of a cement paste in the saturated condition. Apparently, volumetric concentration of crystalline hydrates increases with increasing curing time.

5-3 The Correlation of Shrinkage Speed and Drying Speed

Mean speed of shrinkage and weight loss was calculated from each increment of the measurements, and this mean value was assumed to represent the speed at the middle of the corresponding time increment. Figures 11 through 15 were obtained by

plotting the speeds against drying time in log-log scale.

Four or five different transition points were observed in common with all specimens except for those cured for 122 days.

Transition A: This transition was observed within 1 day from initiation of drying and was distinct especially for poorly-cured specimens. Drying speed of those specimens remained essentially constant and shrinkage speed decreased tracing a decay curve of higher order until this point. After this transition, shrinkage speed increased until a maximum point *A'* was reached. As the curing time of a specimen increases, this increase in shrinkage speed became

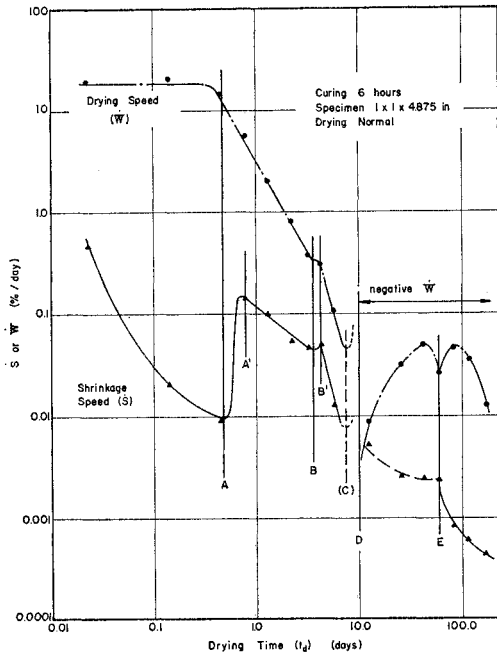


Fig. 11 Shrinkage Speed and Weight Loss Speed vs. Drying Time (6 hours of Curing)

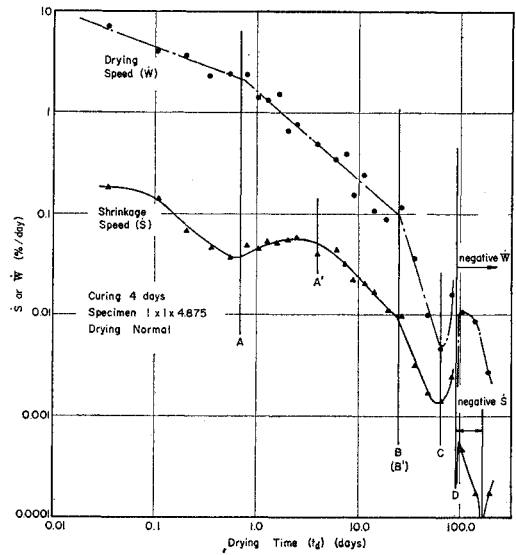


Fig. 13 Shrinkage Speed and Weight Loss Speed vs. Drying Time (4 Days of Curing)

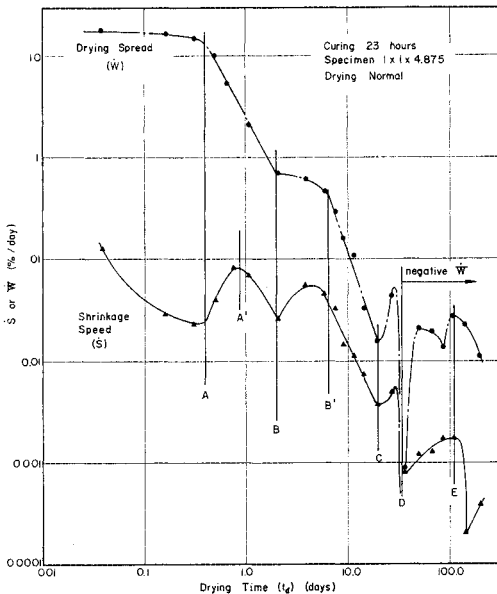


Fig. 12 Shrinkage Speed and Weight Loss Speed vs. Drying Time (1 Day of Curing)

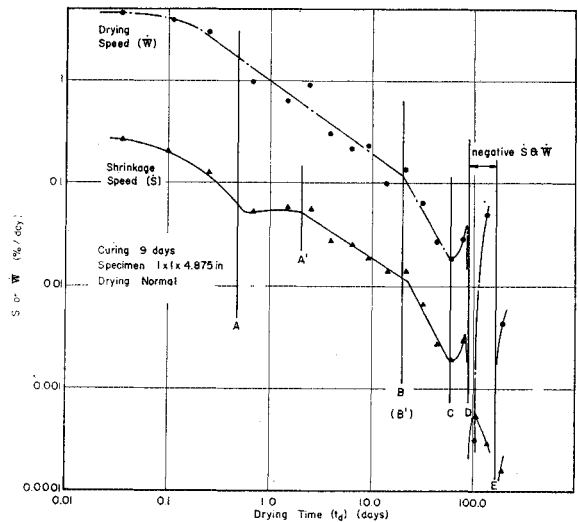


Fig. 14 Shrinkage Speed and Weight Loss Speed vs. Drying Time (9 Days of Curing)

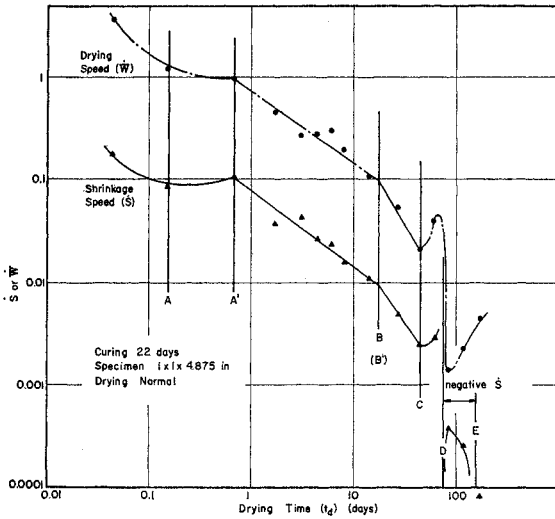


Fig. 15 Shrinkage Speed and Weight Loss Speed vs. Drying Time (22 Days of Curing)

less obvious and took more time. After A' is reached, shrinkage speed decreased linearly with increasing drying time. This line can be written as

$$\dot{S} = At_d^{-\alpha} \dots\dots\dots (7)$$

where

\dot{S} = shrinkage speed,

t_d = drying time,

A, α = constants.

Drying speed decreased linearly from A to B , and also can be formulated as

$$\dot{W} = Bt_d^{-\beta} \dots\dots\dots (8)$$

where

\dot{W} = drying speed,

B, β = constants.

Transition B : Transition from A to B is caused by a sudden increase in α and β of equations (7) and (8). For poorly-cured specimens, especially for those cured for 1 day, this transition did not occur simultaneously, as is shown as the region B to B' . In this region, \dot{W} remained more or less constant and \dot{S} increased again. Except for this region, equations (7) and (8) are also applicable for the region between B and C . Substantial amount of shrinkage occurred in between A and C .

Transition C : Transition C was common to all specimens except those cured for 6 hours. At this point both \dot{S} and \dot{W} began to increase and after reaching a maximum point abruptly decreased again following transition D .

Transition D : Weight increase took place through this transition point, and \dot{S} decreased discontinuously. Effect of this transition became less prominent as the curing time is increased. For those specimens cured for 22 days sudden decrease in \dot{W} was only observed. This might be caused by non-uniform distribution of evaporation and carbonation across

the section. This non-uniformity became more and more pronounced with increasing curing time of a specimen.

Transition E : A transition like point was observed after D , but its effect on measurements was not consistent. This transition will be discussed in section 5-5.

These transition points may be interpreted physically as follows. When the water in macropores is evaporated, evaporation of physically bound water will break out to cause transition A . Until this point, \dot{W} was constant in Figures 15 and 16, which possibly means that evaporation surface remains constant and capillary flow supplies as much water as is evaporated. This type of void may be emptied from the center of a specimen and the water-filled capillary zone which exhibits driving force for shrinkage according to the Kelvin equation is distributed from the surface to some depth that reduces to zero when the point A is reached. This is presumably why \dot{S} showed a decay curve of higher order towards transition A . This transition was used to differentiate combined water for poorly-cured specimens (5-2).

After A transition, hydrostatic tension was set up in the first step gel pores (called A pores) which may be discontinuously small in diameter compared to that of capillary pores. Therefore forces between structures increased abruptly causing sudden increase in inelastic and may be some elastic deformation as is clearly seen in Figures 11 and 12. The change in the amount of this increase and time lag to reach the maximum point (A') with curing time of each specimen, may be caused by the change in the degree of inelasticity and contribution of cross sectional effect. The reason why the equations (7) and (8) hold for the region A' to B and A to B respectively is not certain.

Essentially a similar phenomenon to that occurred in the region A to B may be occurring in the region B to C . The only difference might be discontinuously small diameter of gel pores for this region (called B pores). When the point B is reached, destruction of menisci in A pores takes place. As the destruction of menisci causes increase in evaporation speed, more or less constant \dot{W} from B to B' observed in Figures 11 and 12 may be explained by this. Increase in \dot{S} may be caused by the same mechanism as that occurred just after A transition. The region B to B' was more narrow in Figure 11 than in Figure 12. As will be discussed later concentration of B pores is less for poorly-cured specimens and this is probably the reason. For those specimens cured more than 4 days, the region B to B' was not observed. For such specimens the destruction of A pore menisci must have occurred all the way along

A to B due to the cross sectional non-uniformity, and this may also explain rather violent scatter in data in this region.

For the region B to C, less scatter was observed. Probably, capillary pores and already vacant A pores provided evaporation path for B pore water to evaporate and cross sectional effect was not so serious for this region.

At transition point C, destruction of B pore meniscuses might have started and \dot{W} and \dot{S} increased. Destruction of meniscuses probably leads to subsequent wetting of water on crystal surfaces, and effective evaporation surface may be increased by substantial amount. The void spaces created by the destruction may further act as evaporation path. This may be why destruction of meniscuses results in increase in \dot{W} .

Once the wetted layer of water is evaporated, contact area between cement and air increases substantially and carbonation process is promoted giving rise to D transition soon after the maximum \dot{W} is observed.

The suggestion about the possible existence of two different size pores coincides with the observation done by Verbeck¹⁰⁾ and Reper¹²⁾ individually.

Weight losses in terms of cement weight (W_c) at which these transition occurred, were tabulated in Table 2. These values were plotted against curing time in Figure 16. The lines corresponding to A, C, D transitions were approximately parallel, which

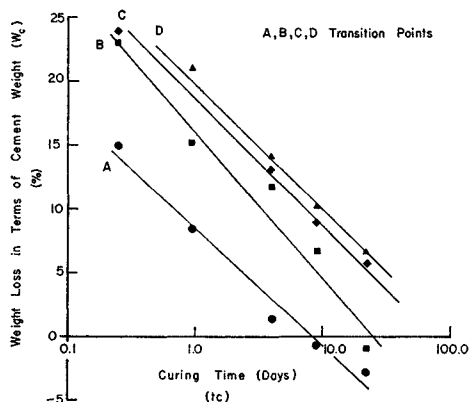


Fig. 16 Transition Points vs. Curing Time.

Table 2 Transition Points Indicated by Weight Loss in Terms of Cement Weight (W_c)

Type of Transition	6 hours	23 hours	Curing time 4 days	9 days	22 days
A	15.0	8.4	1.40	-0.80	-2.80
A'	17.6	12.2	6.20	1.00	-2.00
B	23.0	15.2	11.80	6.60	-1.00
B'	23.3	28.0			
C	(23.8)	20.8	13.00	8.80	5.60
D	24.0	21.0	14.00	10.20	6.60
E	21.8	17.0	13.20	9.80	7.00

suggests that the evaporable amount of physically combined water at 50% R.H. remains constant regardless of curing condition. The slope of B transition suggests that transformation of A pore water into B pore water is taking place with increasing curing time. Probably B pores are created by interlocking or dendritic growth of tobermorite crystals between main structures that compose A pores.

5-4 Expansion due to Destruction of Meniscuses

In Figures 7 and 8, sudden expansion indicated by a circle was observed with increasing weight loss for poorly-cured specimens. This expansion took place twice for specimens cured for 1 day and once for those cured for 10 hours. For other specimens this expansion did not appear.

These singular points obtained from series 3 were compared to the transition points, observed in series 1 and discussed in the previous chapter, in Table 3. Considering the effect of cross sections which were different for series 1 and series 3, these points can be regarded as equivalent to the transition points observed in series 1. For 10 hours specimens this point corresponds to transition B and for 1 day specimens point 1 and 2 correspond to transition B and C respectively.

Those expansions may be considered as elastic spring back of cement structure due to the destruction of meniscuses. Here arises a question why, in the previous chapter, \dot{S} increased just after transition B and C, because \dot{S} is expected to decrease due to this type of expansion.

This is partly explained by overlapping the effect of the increased hydrostatic tension of the next step gel pores, but this does not explain completely why this expansion took place only in series 3. Probably T.C. Powers' suggestion²⁰⁾ that the hydrostatic tension exceeds the fracture strength of water at relative vapour pressures below 0.45, may be related to this phenomenon as the series 3 experiment was carried out at almost 0% relative humidity.

Table 3 Comparison of Destruction Point of Meniscuses to Transition Points

Specimen size	Curing time	10 hours	1 Day		
			point 1	point 2	
1" x 3/8"	W_c (%)	22.2	21.2	23.8	Series 3
	ΔS (%)	0.06	0.03	0.04	
1" x 5/8"	W_c (%)	21.2	18.5	22.0	Series 3
	ΔS (%)	0.02	0.02	0.02	
		transition B	transition B	transition C	
1" x 1"	W_c (%)	19.2	15.2	20.8	Series 1

5-5 Carbonation and its Effect on Shrinkage

It is clear that the carbonation process becomes

Table 4 Signs of \dot{S} and \dot{W} Before and After E Transition

Curing time t_c	\dot{S}		\dot{W}	
	D to E	After E	D to E	After E
6 hours	P	P	N	N
23 hours	P	P	N	N
4 days	N	P	N	N
9 days	N	P	N	P
22 days	N	P	P	P

P.....positive
N.....negative

operative after D transition, and the data showed some discontinuity in this carbonation region which was temporarily designated as E transition. Physical changes caused by this transition were not consistent, however, for different curing time of specimens even in a qualitative sense. Table 4 shows how the signs of \dot{S} and \dot{W} before and after E transition are changed with curing time.

For those specimens cured more than 4 days the negative sign of \dot{S} was reversed through E transition, that is, the expansion which was taking place from D to E was substituted by contraction after E transition. For 22 day of curing, weight increase was not observed and the negative \dot{W} from D to E for 9 days specimens changed into positive again through E transition. This fact is important because it is not that positive \dot{W} reversed into negative \dot{W} .

Possibly the negative \dot{S} before E transition could be explained by the destruction of B pore menisci which took place successively from C to E transition because of great sectional effect of such specimens which could also be the reason for positive \dot{W} of old specimens.

The intervention of the negative \dot{W} zone from D to E for 9 days of curing possibly suggests that carbonation process could be saturated while consistent evaporation is going on, or the idea of stepwise carbonation as was predicted as A pore to B pore switch in evaporation could also be applied.

5-6 Effect of Specimen Size

Relative position of the curves in shrinkage weight loss plot was not much influenced by specimen size. Therefore, the discussion in section 5-2 may be not much influenced by specimen size.

For the smaller size specimens, shrinkage and weight loss observed within less than 3 days were greater than those obtained for the larger sizes of specimen and effect of carbonation manifested itself after shorter drying time. Shrinkage after the carbonation took place was less for a smaller size of specimen and the total shrinkage was also less for smaller specimens by this effect, though the amounts of the maximum weight loss and subsequent weight increase by carbonation corresponding to each curing

condition were not much influenced by specimen size. This fact together with the discussion in section 5-5 strongly suggests that the carbonation might not be an immediate cause of shrinkage. It is also expected that the discussion in section 5-3 will be considerably affected by the specimen size.

6. CONCLUSIONS

1. As is shown in Figure 8, shrinkage of cement paste is considered to be a function of its maturity. The maximum shrinkage, twice as large as that obtained for 122 days of curing, was observed for 4 days of curing.

2. The amounts of combined water were deduced from linear portion of shrinkage weight loss curves for each curing condition. As is shown in Figure 9, reaction rates thus measured showed linearity with curing time in log-log scale and concurred fairly well with the theoretical rates of hydration calculated from a set of chemical equations proposed by Brunauer and Copeland. For the two cases, the equations (2) and (3) were obtained by the least square method. The form of these equations indicated that hydration process of cement can be discussed in terms of the reaction rate theory by identifying the curing time from mixing as the reaction time.

3. The amount of physically bound water determined as the difference between the equation (4) and (5) remained essentially constant after setting of cement as is shown in Figure 10.

4. The amounts of self-desiccation were predicted for various curing time from the same chemical equations to give the results shown in Figure 2. Self-desiccation up to 8 to 10% of paste volume can occur even for the practical values of W/C ratio. Sensitivity of the self-desiccation of a particular cement is indicated by the equation (1).

5. By plotting shrinkage speed and weight loss speed against drying time in log-log scale, four or five transition points were observed in common with all curing conditions up to 22 days as is shown in Figures 11 to 15. Physical interpretation of these transition points was attempted in section 5-3, and the structural model proposed in section 2-2 was indirectly supported by this discussion.

6. For wide variations of drying time, the experimental equations (7) and (8) can be applied to describe shrinkage speed and weight loss speed of cement paste. An abrupt change in α and β of the equations (7) and (8) at B transition was probably caused by the initiation of evaporation of a second type of physically bound water. The first type (A) may be located in larger pore sizes and this second type (B) in smaller sizes. The idea of discontinuous pore size is in accord with recent publications. By

comparing the transition points obtained for various curing time collectively, it was suggested that the transformation of *A* pore into *B* pore may be occurring with increasing curing time of cement paste.

7. It is quite doubtful that carbonation causes shrinkage of cement paste. Carbonation process and its effect on shrinkage will be different if the degree of hydration of specimens is different. Table 4 summarizes the effect of curing time on carbonation. As is shown in Figures 13 and 14, expansion was observed as the carbonation took place. It was also suggested that there might be two different stages in carbonation process connected by *E* transition.

8. Sudden expansion, which took place with increasing weight loss in Figures 7 and 8 on those specimens subjected to a desiccant drying of magnesium perchlorate, is explained by an elastic spring back of cement structure when meniscuses disappeared suddenly from interstitial space. Each singular point can be corresponded to the transition point predicated from \dot{S} and \dot{W} plot, as is shown in Table 3.

9. Sectional non-uniformity increased with increasing curing time and drying speed, as was discussed in section 5-3. Self induced residual stress will be very impotent for crack prevention.

10. Shrinkage is not always greater for smaller size specimens as is observed in Figures 4, 5 and 6. Effect of specimens size on shrinkage and weight loss is not simply understood. Specimen size, however, might have some influence on conclusions 1, 5, and 6. The conclusion 2 may not be much influenced by specimen size.

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9. LIST OF NOTATION

A, *B*=constants

α , β =constants

F=capillary tension force

M=molecular weight of water

M_a=specific moles of C₃S per gram of cement

M_b=specific moles of C₂S per gram of cement

M_c=specific moles of C₄AF per gram of cement

M_d=specific moles of C₃A per gram of cement

M_e=specific moles of CaSO₄·2H₂O per gram of cement

P=the existing vapour pressure over a concave surface

P_s=vapour pressure over plane surface at temperature *T*, the saturated vapour pressure

r=principal radii of water surface curvature

R=gas constant

S =uni-axial shrinkage strain (%)
 S_c =volumetric shrinkage due to the chemical reaction (%)
 \dot{S} =uni-axial shrinkage speed (%/day)
 T =absolute temperature
 t_c =curing time (day)
 t_d =drying time (day)
 v_f =specific volume of water
 W =weight loss in terms of paste weight (%)
 W_c =weight loss in terms of cement weight (%)
 \dot{W} =weight loss speed (%/day)

$(W/C)_m$ =measured value of combined water per gram of cement
 $(W/C)_c$ =calculated value of combined water per gram of cement
 $(W'/C)_m$ =measured value of hydration rate
 $(W'/C)_c$ =calculated value of hydration rate
 $(W/C)_{ph}$ =physically combined water per gram of cement
 σ =surface tension of water

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