Mixture Proportioning for Internal Curing

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The concept of internal concrete curing is steadily progressing from the laboratory to field practice.[1,2] In terminology currently being considered by ACI Committee 308, Curing Concrete, "internal curing refers to the process by which the hydration of cement occurs because of the availability of additional internal water that is not part of the mixing water." The additional internal water is typically supplied by using relatively small amounts of saturated, lightweight, fine aggregates (LWA) or superabsorbent polymer (SAP)[3] particles in the concrete.[4] Benefits of internal curing include increased hydration and strength development, reduced autogenous shrinkage and cracking, reduced permeability, and increased durability.[2,4] The impact of internal curing begins immediately with the initial hydration of the cement, with benefits that are observed at ages as early as 2 days.[2]

Internal curing is especially beneficial in low water-cement ratio (w/c) concretes because of the chemical shrinkage that accompanies portland cement hydration and the low permeability of the calcium-silicate hydrates. Because the water that is chemically bound and adsorbed by the cement hydration products has a specific volume less than that of bulk water, a hydrating cement paste will imbibe water (about 0.07 g water/g cement) from an available source.[5] While in higher w/c concretes, this water can be, and often is, supplied by external (surface) curing, in low w/c concretes, the permeability of the concrete quickly becomes too low to allow the effective

transfer of water from the external surface to the concrete interior.[6] This is one justification for internal curing. Additional water that can be distributed somewhat uniformly throughout the concrete will be more readily able to reach unhydrated cement.

REQUIRED INTERNAL CURING WATER

How much lightweight aggregate is needed to supply water for internal curing of any given concrete mixture? Bentz and Snyder[6] have previously published an equation for calculating this:

$$M_{LWA} = \frac{C_f \times CS \times \alpha_{max}}{S \cdot \times \phi_{LWA}} \qquad (1)$$

where:

M_{LWA} = mass of (dry) fine LWA needed per unit volume of concrete (kg/m^3 or lb/yd^3);

C_f = cement factor (content) for concrete mixture (kg/m^3 or lb/yd^3);

CS = chemical shrinkage of cement (g of water/g of cement or lb/lb);

α_{max} = maximum expected degree of hydration of cement;

S = degree of saturation of aggregate (0 to 1) (Note: Eq. (1) is only valid for non-zero values of S, as otherwise the amount of LWA needed diverges to infinity.); and

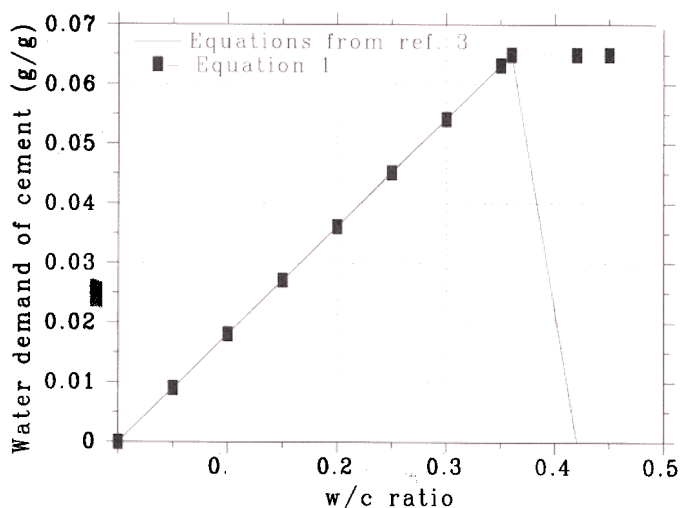ϕ_{LWA} = absorption of lightweight aggregate (kg water/kg dry LWA or lb/lb).

Fig. 1: Internal water needed to maintain saturated conditions in cement paste (CS = 0.065)

For w/c below 0.36, the maximum expected degree of hydration of the cement under saturated conditions can be estimated as ($[w/c]/0.36$) and should not vary significantly with curing temperature.[7] For w/c higher than 0.36, the maximum expected degree of hydration of the cement can be estimated as 1. Because the densities of the dry lightweight aggregates and the conventional aggregates are substantially different, the ultimate substitution in the concrete mixture should be performed on a volume basis with the determined mass of LWA from Eq. (1) replacing the same volume of conventional aggregates. Knowing the dry densities of the two types of aggregates, a simple calculation can be employed to determine the mass of conventional aggregates that must be removed from the mixture (which will be more than the mass of the LWA determined by Eq. (1)). As an example of applying Eq. (1), a concrete mixture with a cement factor of 450 kg/m³ (760 lb/yd³), a chemical shrinkage of 0.07 g water/g cement, and an aggregate absorption of 15% at complete saturation would require 193 and 210 kg/m³ (325 and 350 lb/yd³) of LWA for w/c of 0.33 and 0.40, respectively.

Substituting the relationship between w/c and maximum expected degree of hydration into Eq. (1) yields a linear relation between internal water demand of the cement ($CS \times \alpha_{max}$ in Eq. (1)) and w/c up to a w/c of 0.36 (Fig. 1). For a w/c less than 0.36, the relation is the same as that proposed by Jensen and Hansen.[3] For w/c greater than 0.36, the internal water demand reaches a plateau value equivalent to the chemical shrinkage of the cement (CS = 0.065 in Fig. 1). For a w/c greater than 0.36, this relation differs substantially from that proposed by Jensen and Hansen.[3] For a w/c between 0.36 and 0.42, they proposed adding sufficient water only to complete

the hydration of the cement, while Eq. (1) proposes adding enough water to keep the pores in the cement paste completely saturated. These represent two extreme views and the actual optimum in terms of performance may lie somewhere between the two lines shown in Fig. 1.

Equation (1) always estimates internal curing water needed to maintain complete saturation within the hydrating cement paste by exactly compensating for the chemical shrinkage of the hydrating cement paste in the concrete mixture at the maximum expected degree of hydration. While it can be applied to higher w/c (> 0.45) concretes with degrees of saturation (S) of less than one, it does not address the potential problems in rheology and bleeding that might result in such an application due to having an extremely wet mixture. For these higher w/c concretes, it may be much more efficient and practical to supply curing water via conventional means such as misting or the use of wet burlap. Even when internal curing is used, however, loss of water from the surface must be minimized to allow for dense cover concrete to be obtained. This applies for all types of concrete.

This article presents refinements for estimating the parameters in Eq. (1) that will provide a readily recognized means of choosing the proper amount of LWA and improve mixture proportioning via this method. The two major factors to be considered are: 1) the variation of CS with portland cement phase composition and curing temperature, and 2) the relevant value for the absorption (or more appropriately desorption) of the lightweight aggregate. Taken together, expected variations in these factors could result in an underestimation of the quantity of internal curing water by over 30% according to Eq. (1). After addressing these concerns, a procedure for mixture proportioning for internal curing is recommended.

CHEMICAL SHRINKAGE

While no standard U.S. method exists for evaluating chemical shrinkage, it can be directly measured using either a gravimetric[5,8] or a volumetric method.[5,9,10] A relatively simple standard test method is currently being balloted by the ASTM C01.31 Volume Change subcommittee (Japan already has one).[11] Because a value for the long-term chemical shrinkage is desirable for internal curing calculations, an alternative to measurement is to calculate it based on the phase composition of the cement.

Knowing the molar volumes of all relevant cement phases (as provided in Table 1)[9,12,13] and the expected cement hydration reactions,[9,14] the chemical shrinkage due to the hydration of each of the principal cement clinker phases can be calculated.[8] A volume balance is performed on each (molar) balanced hydration reaction, and the chemical shrinkage is computed as the difference in volumes between the hydration products and the

TABLE 1:
Densities and molar volumes of cementitious materials at 25 °C (77 °F)

Phase	Density, Mg/m³	Molar volume, cm³/mole
C_3S	3.21	71.1
C_2S	3.28	52.5
C_3A	3.03	89.1
C_4AF	3.73	130.3
Gypsum (dihydrate)	2.32	74.21
Hemihydrate	2.74	52.97
Anhydrite	2.61	52.16
Silica fume	2.22	27.0
CH (portlandite)	2.24	33.08
$C_{1.7}SH_{4.0}$	2.11	107.8
C_3AH_6	2.52	150.12
$C_6A\bar{S}_3H_{32}$ (ettringite)	1.7	735.0
$C_4A\bar{S}H_{12}$	1.99	312.8
FH_3	3.0	69.8
H (water)	0.9971	18.07

Note: 1 Mg/m³ = 1700 lb/yd³; 1 cm³ = 0.061 in.³
Typical cement chemistry notation is used throughout this article C = CaO, S = SiO$_2$, A = Al$_2$O$_3$, F = Fe$_2$O$_3$, S̄ = S̄O$_3$, and H = H$_2$O.

TABLE 2:
Calculated coefficients for chemical shrinkage due to cement hydration

Cement phase	Coefficient, g water/g solid cement phase
C_3S	0.0704
C_2S	0.0724
C_3A	0.171[*] 0.115[†]
C_4AF	0.117[*] 0.086[†]
Silica fume	0.20

[*]Assuming sufficient sulfate to convert all of the aluminate phases to ettringite
[†]Assuming total conversion of the aluminate phases to monosulfate

TABLE 3:
Calculated chemical shrinkage for CCRL proficiency cement samples

Cement phase	Phase mass fractions (via SEM imaging)	
	CCRL 135	CCRL 140
C_3S	0.616	0.595
C_2S	0.160	0.167
C_3A	0.0604	0.0852
C_4AF	0.0887	0.0664
Chemical shrinkage, g water/g cement	0.0695[*]	0.0763[†]

[*]Assuming total conversion of the aluminate phases to monosulfate
[†]Assuming sufficient sulfate to convert all of the aluminate phases to ettringite

reactants (including water), normalized by the molar mass of the specific cement clinker phase being considered. By assuming a density of 1.0 g/cm³ for water, the final units of g water/g cement clinker phase are obtained. Table 2 lists typical chemical shrinkage coefficients for four cement phases and silica fume. For the aluminate phases, the exact value depends strongly on the sulfate content of the cement and the resulting balance between the formation of ettringite (high sulfate content) and the monosulfoaluminate phase (lower sulfate content).

The Table 2 coefficients are strongly sensitive to the values chosen for the densities of the different phases given in Table 1, and other authors have thus calculated values differing from those in Table 2.[8,15] The values given here, however, are those historically and currently used in the Virtual Cement and Concrete Testing Laboratory (VCCTL) system,[7] whose prediction of measured chemical shrinkage has been verified on a wide variety of portland cements.[9,10,16]

The expected chemical shrinkage of any portland cement can be calculated based on the mass composition of the cement and the chemical shrinkage coefficients in Table 2. Table 3 illustrates the results of applying this calculation procedure to two recent Cement and Concrete Reference Laboratory (CCRL) proficiency cement samples.[17,18] There is about a 10% difference in the calculated chemical shrinkage for these two cements.

A further complication with respect to predicting chemical shrinkage is the expected curing temperature. Geiker[5] first observed that the ultimate chemical shrinkage is significantly reduced at elevated curing temperatures. The observed magnitude of this effect was on the order of 0.0005 (g water/g cement) per degree Celsius in the temperature range of 12 to 50 °C (54 to 120 °F).[5] For comparison, data for chemical shrinkage versus degree of hydration at temperatures between 10 and 50 °C (50 and 120 °F) presented by Mounanga et al.[8] yield a coefficient of approximately 0.0008 (g water/g cement)/°C.

TABLE 4:
### "PROTECTED PASTE" VOLUME AS A FUNCTION OF DISTANCE FROM THE LWA SURFACES

Distance from LWA surface, mm	Protected paste fraction
0.02	0.046
0.05	0.128
0.1	0.280
0.2	0.563
0.5	0.978
1.0	1.000

Note: 1 in. = 25.4 mm.

Accepting the values given in Tables 1 through 3 as being those for a nominal curing temperature of 25 °C (77 °F) and taking a conservative approach to the influence of temperature, calculated values for chemical shrinkage (such as those in Table 3) should be reduced by 0.005 g water/g cement for each 10 °C (18 °F) that the average expected curing temperature is above 25 °C (77 °F). Conversely, they should be increased by 0.005 g water/ g cement for each 10 °C (18 °F) that the average curing temperature is below 25 °C (77 °F). For curing temperatures in the range of 5 to 35 °C (40 to 95 °F), the magnitude of this effect is on the order of 25%. For steam curing and larger field structures (where temperatures can reach up to 60 °C [140 °F]), the effect would be even more significant.

AGGREGATE ABSORPTION (DESORPTION)

How much of the water in lightweight aggregates is readily available to migrate to the hydrating cement paste during curing? It is incorrect to assume that all of the water in the LWA will be available.[10,19] A more reasonable approach is to prewet the aggregates so the moisture condition is similar to that of aggregates used in trial batches, and then measure how much water is released at a reduced relative humidity. As low w/c cement paste hydrates under sealed conditions, the internal relative humidity (RH) can drop to the range of 85 to 90%.[10] As water surrounding an initially saturated LWA migrates to a nearby hydrating cement particle, LWA-absorbed water replaces the migrating water, maintaining saturated conditions within the hydrating cement paste, and developing unsaturated conditions within the LWA particles.[10] For the water in the LWA to effectively participate in hydration, it must surely be released from the LWA before these RH levels of 85 to 95% are reached internally.
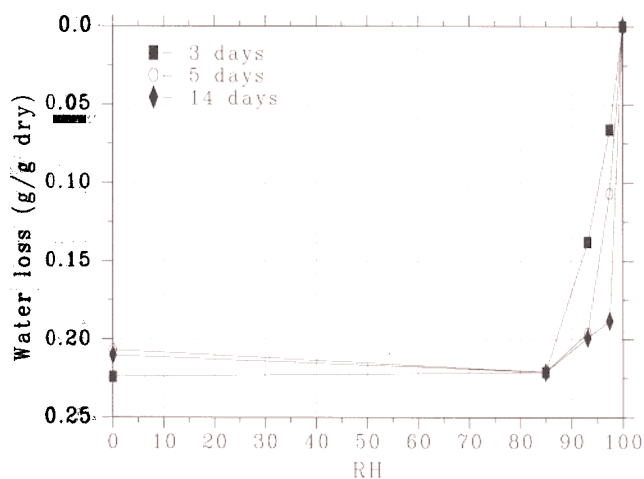
Fig. 2: Desorption isotherm versus relative humidity (RH) and exposure time for Hydrocure® LWA. RH values of 97, 93, and 85% were obtained using saturated salt solutions of potassium sulfate, potassium nitrate, and potassium chloride, respectively. RH of 0% was obtained with 40 °C (100 °F) oven drying followed by placement in a desiccator with a desiccant

To characterize the absorption of the aggregates (ϕ_{LWA}) at complete saturation (S = 1), saturated LWAs can be conveniently exposed to environments with known equilibrium RH that are maintained via saturated salt solutions. The water desorbed from the LWA in these exposures provides the value for ϕ_{LWA} (at S = 1) that should be used in Eq. (1). Exposures to saturated salt solutions of potassium sulfate and potassium nitrate provide equilibrium RH of about 97 and 92% at 25 °C (77 °F), respectively.[10] Thus, use of the potassium sulfate solution could be viewed as a conservative approach to internal curing, while a potassium nitrate solution should provide a more liberal estimate.

Figure 2 shows representative desorption isotherms for an expanded shale lightweight aggregate,* measured at a temperature of 20 °C (70 °F) at the National Institute of Standards and Technology (NIST). From Fig. 2, it can be observed that a minimum of a 1- to 2-week exposure to the saturated salt solution may be necessary to obtain an equilibrium mass for the "saturated" LWA, based on exposing 2 to 3 g (0.07 to 0.11 oz.) samples of saturated LWA to the salt solutions. This particular LWA loses over 95% of its absorbed water at an RH as high as 93%, a beneficial characteristic for its application in internal curing. Not all candidate LWA materials have this desirable property, with some LWAs losing as little as 50 to 80% of their absorbed water at an RH as low as 84%.[19] An alternative

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* Certain commercial products are identified in this article to specify the materials used and procedures employed. In no case does such identification imply endorsement by NIST or ACI, nor does it indicate that the products are necessarily the best available for the purpose.

to measuring desorption isotherms for the LWA may be to measure the cumulative absorption over different time intervals, as the rate of absorption may relate to the ease of desorption.[2]

RECOMMENDED PROCEDURE FOR DETERMINING AMOUNT OF LWA NEEDED

1. Obtain the mass composition of the cement clinker from either a detailed scanning electron microscope (SEM)/X-ray image analysis[7] or the Bogue calculation.
2. Calculate the expected chemical shrinkage (CS) of the cement at 25 °C (77 °F) using the coefficients provided in Table 2 (and considering the availability of sulfate for the aluminate phase reactions).
3. If the expected average curing temperature is above 25 °C (77 °F), decrease the calculated value by 0.0005 per °C above 25 °C (77 °F).
4. If the expected average curing temperature is below 25 °C (77 °F), increase the calculated value by 0.0005 per °C below 25 °C (77 °F).
5. Measure the desorption of the LWA from a saturated state down to an RH of relevance for the internal curing of concrete. Saturated salt solutions of potassium sulfate and potassium nitrate, for example, can be used to obtain equilibrium RH values of about 97 and 92% (at 25 °C [77 °F]), respectively. If desired, a safety factor can be applied to account for the variability in the absorption of the LWA, if multiple measurements of desorption are performed to estimate this factor.
6. Substitute the determined values for CS and ϕ_{LWA} in Eq. (1) to obtain the desired mass of lightweight fine aggregate in the concrete mixture.

ADDITIONAL CONCERNS

Naturally, other physical properties of the LWA such as mechanical strength, particle shape, and particle grading will influence properties of both the fresh and hardened concrete. To optimize the performance of the LWA in the concrete system, these properties should be as similar as possible to those of the normalweight sand being replaced by the LWA.[2]

Internal curing water must be distributed uniformly throughout the concrete. This is especially important for curing at later ages, when the distance the water can travel may become limited to hundreds of micrometers due to the ever-decreasing permeability of the hydrating cement paste.[6] A more uniform distribution of internal curing water is best achieved by the use of fine (as opposed to coarse) lightweight aggregates (or SAP particles, which are on the order of hundreds of micrometers in diameter[3]). The actual projected distribution of water availability for a given concrete mixture with saturated lightweight aggregates, based on a hard core/soft shell
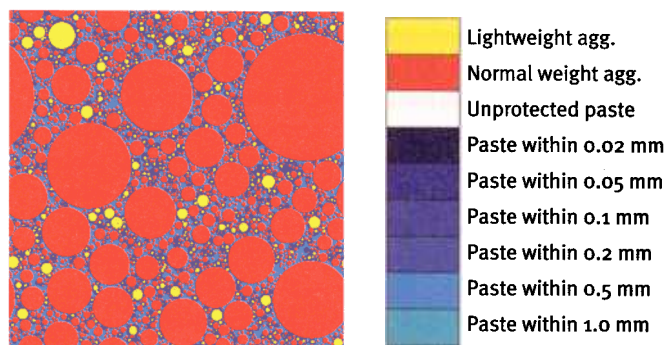

Fig. 3: Example two-dimensional image (30 x 30 mm) from internal curing simulation. Note: 1 in. = 25.4mm

(HCSS) microstructural model developed at NIST,[20] can be computed and viewed using a website available at **http://ciks.cbt.nist.gov/1wagg.html**. At this site, the user provides the aggregate gradation, lightweight aggregate replacement fraction, and overall aggregate volume fraction and the system returns a representative color-coded two-dimensional image from the "virtual" concrete along with a table indicating the protected paste volume fraction[6] as a function of distance from the surfaces of the LWA particles.

An example of the model output for a concrete with 70% aggregates by volume and replacement of 20% of the fine aggregates by LWA is provided in Fig. 3 and Table 4. In this example, while 100% of the cement paste is within 1.0 mm (40 mil) of a LWA surface (a relevant distance for early age curing), only 56% of the cement paste is within 0.2 mm (8 mil) of a LWA surface (a more relevant distance for later age curing).[21]

This previously stated methodology has been developed for concrete mixtures based on ordinary portland cement. The use of blended cements (with silica fume, slag, fly ash, and the like) will require further modifications to the computation of chemical shrinkage and "internal water demand." These blending components influence both the kinetics of hydration and the absolute volume of chemical shrinkage.[10] Further research on these materials is needed to provide a quantitative basis for extending the presented methodology to cover them.

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