LWA absorption and desorption: the influence on the microstructure and transport properties of internally cured mortars

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**ABSTRACT:** This study examines the influence of internal curing on absorption of water and heat of hydration in mortar specimens. In addition, procedures for determining the absorption and desorption of LWA are also discussed, as this can play a substantial role in determining the volume of LWA that is needed and the amount of curing water that can be supplied to the paste. The results indicate that the inclusion of water-filled LWA can increase the long term degree of hydration of the cement paste and reduce both the total porosity and the interconnection of the pore structure of mortar specimens. The sorptivity results for an internally-cured mortar with a w/c of 0.30 indicate performance that is consistent with a conventional mortar prepared with a w/c of 0.23 or a paste with a w/c of 0.30.

1 **INTRODUCTION**

Internal curing uses water-filled inclusions (typically lightweight aggregate, LWA) to provide sacrificial water-filled reservoirs to supply water on demand to the hydrating cement paste from the time of mixing until the time when moisture equilibrium is achieved between the reservoirs and the surrounding cement paste (Bentz & Snyder 1999, Jensen & Hansen 2001, Bentz et al. 2006, Kovler & Jensen 2007, Radlinska 2008). This allows the fluid in the lightweight aggregate to be transferred to the paste thereby reducing self-desiccation in the paste along with its accompanying autogenous shrinkage, and thus avoiding early-age cracking (Lura 2001, Mohr 2005, Henkensiefken 2008a, b, Henkensiefken et al. 2009a).

Previous work (Bentz 2006, Bentz & Sturzman 2008, Henkensiefken et al. 2009b) has shown that the use of LWA for internal curing will increase the long term degree of hydration of sealed cured mortars, producing a denser microstructure. Bentz et al. (1999) and Bentz (2009) suggested that this densification around the aggregates results in a system with less percolated normal weight aggregate (NWA) interfacial transition zones (ITZs) and therefore could provide a further reduction in sorptivity and fluid transport. Elsharief et al. (2005) and Peled et al. (unpublished) used scanning electron microscopy (SEM) to show a reduction in the porosity of the zone surrounding the LWA in comparison with NWA. Peled et al. (unpublished) used an atomic force microscopy technique (AFM) to further confirm the densification of the ITZ and the reduction in calcium hydroxide near the surface of the LWA.

One fundamental concept in the proportioning of mixtures with internal curing is determining the volume of the lightweight aggregate (i.e. volume of the water reservoirs that are needed). A straightforward approach has been developed to estimate this volume of water based on the concept that all of the created chemical shrinkage volume will be replaced by water. This concept has been proposed by Bentz et al. (1999) and Bentz et al. (2005) and is shown in Equation 1:
\[ M_{\text{LWA}} = \frac{C_f \times CS \times \alpha_{\text{max}}}{S \times \Phi_{\text{LWA}}} \]  

where: \( M_{\text{LWA}} \) (kg/m\(^3\)) is the mass of LWA (in a dry state) that needs to be saturated to provide sufficient water to fill in the voids created by chemical shrinkage, \( C_f \) (kg/m\(^3\)) is the cement content of the mixture, \( CS \) (g of water per g of cement) is the chemical shrinkage of the cement, \( \alpha_{\text{max}} \) (unitless) is the expected maximum degree of hydration (0 to 1), \( S \) (unitless) is the expected degree of saturation of the LWA (0 to 1) and was taken to be 1 in this study when the dry LWA was soaked for 24 h, and \( \Phi_{\text{LWA}} \) (kg of water/kg of dry LWA) is the absorption capacity of the LWA (taken here as the 24 h absorption value). It has been stated that it may be more appropriate to use the desorption of the LWA down to 92 % RH rather than the absorption (Bentz et al. 2005).

It can be noted that to assess correctly the effect of internal curing agents (as LWA) an accurate determination of absorption capacity is crucial. It may also be argued that in addition to just knowing the absorption capacity (i.e., how water can be absorbed by the LWA) it is also vital to know how water is lost from the LWA during curing (i.e., the desorption response). For these reasons, this research will focus on the analysis of available methods to characterize the absorption and desorption behavior of LWA. In addition the effect of internal curing will be measured with respect to transport using electrical impedance (conductivity) and water sorption measurements.

2 RESEARCH SIGNIFICANCE

Specifically this paper considers two main aspects associated with the LWA that is used for internal curing. First, the paper will focus on the challenges and importance of accurate determination of absorption and desorption in the LWA. The need for accurately determining the water that can be absorbed and more importantly desorbed (i.e. given off by the LWA) can clearly be seen in the value of \( \Phi_{\text{LWA}} \) described in Equation 1. Second, this paper will also discuss the beneficial effects of internal curing in terms of increased hydration of the microstructure of the mixture and the densification of the microstructure of the ITZ around the aggregates. This will be discussed in terms of water (Table 1). Three mixtures were cement paste with different \( w/c \), and three mixtures were plain absorption, and degree of hydration.

3 DESCRIPTION OF MATERIAL AND MIXTURES

Eight different mixtures were prepared mortar with a single volume fraction of normal weight aggregate NWA (55 % of the total volume). Two mortar mixtures were prepared with different volumes of NWA replaced by a saturated rotary kilned-expanded shale (from here on, LWA) and a \( w/c \) of 0.30. It is important to note that though the designations (11.0 % and 23.7 %) are on a total volume basis, the volume of aggregate (LWA and sand) remained constant at 55 % since only the sand was replaced with LWA. It should also be noted that 23.7 % volume replacement corresponds to the amount of LWA necessary to compensate for the anticipated chemical shrinkage according to Equation 1.

An ASTM C150 Type I ordinary portland cement (OPC). The normal weight sand used was natural river sand with a fineness modulus of 2.71, an apparent specific gravity of 2.58, and an absorption of 1.8 % by mass. Portions of the normal weight sand were replaced with LWA with a fineness modulus of 3.10 and a specific gravity of 1.56. The 24-hour absorption of the LWA was determined to be 10.5 % according to ASTM C128-07 (ASTM 2007).

The LWA was oven dried, air cooled, and then submerged in water for 24 h ± 1 h prior to mixing. The volume of water used to submerge the LWA included both mixing water and that the water the LWA would absorb in 24 h. The excess water (water not absorbed in 24 h) was then decanted and used as the mixing water. The normal weight sand was oven dried and cooled for 24 h before mixing. For the plain mortar mixtures and the pastes, the water and cement were conditioned for 24 h at room temperature.
Table 1 Mixture Proportions in saturated surface dry (SSD) condition

<table>
<thead>
<tr>
<th>Material</th>
<th>P-0.25</th>
<th>P-0.30</th>
<th>P-0.35</th>
<th>M-0.25</th>
<th>M-0.30</th>
<th>M-0.35</th>
<th>11.0%</th>
<th>23.7%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement (kg/m³)</td>
<td>1761</td>
<td>1619</td>
<td>1498</td>
<td>793</td>
<td>674</td>
<td>728</td>
<td>728</td>
<td>728</td>
</tr>
<tr>
<td>Water (kg/m³)</td>
<td>440</td>
<td>486</td>
<td>524</td>
<td>198</td>
<td>218</td>
<td>236</td>
<td>218</td>
<td>218</td>
</tr>
<tr>
<td>Fine Aggregate (kg/m³)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1418</td>
<td>1418</td>
<td>1418</td>
<td>1135</td>
<td>808</td>
</tr>
<tr>
<td>Dry LWA (kg/m³)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>172</td>
<td>369</td>
</tr>
<tr>
<td>HRWRA (g/100 g cement)</td>
<td>0.60</td>
<td>0.75</td>
<td>0.50</td>
<td>0.60</td>
<td>0.50</td>
<td>0.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water Provided by LWA (kg/m³)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>18</td>
<td>39</td>
</tr>
</tbody>
</table>

4 AGGREGATE ABSORPTION AND DESORPTION

Determining the absorption of the aggregate can be problematic due to difficulties in determining the saturated surface dry (SSD) condition for lightweight aggregate. This paper used three different techniques to evaluate SSD and compared the results. The techniques included the standard cone method (ASTM 2007), the paper towel method, and the use of cobalt chloride (O’Neil & Smith 2001).

It should be noted that ASTM C128 is not intended to be used for determining the absorption of LWA as stated in section 1.3 and 5.5 of the standard (ASTM 2007). However, in lieu of a more appropriate method for determining the absorption of LWA, ASTM C128 is commonly used. In this test the sample is immersed in water for 24 h, after which time the water is decanted and the surface of the aggregate is dried. The difficulty is determining the saturated surface dry condition, i.e., when there is no more surface moisture on the aggregate. To determine the saturated surface dry condition of the fine lightweight aggregate, the damp aggregate is placed in a cone tamped 25 times, and the cone is removed. The cone (and provisional cone) tests rely on the principle of surface tension for determining when the surface moisture disappears. When moisture is still on the surface of the aggregate, surface tension of the water will hold the particles in the form of the cone after the cone is removed. When no moisture is present on the surface, slight slumping of the aggregate cone will occur. The question that arises from using the cone tests is that the LWA is typically manufactured and crushed, resulting in angular aggregate particles. The angularity of the aggregate could lock the particles together such that when the cone is lifted, the shape is retained even after surface moisture is gone.

The paper towel method involves immersing the aggregate in water for 24 h, after which the water is decanted and the surface of the aggregate is patted dry. The paper towel method involves spreading the aggregate and touching a paper towel to the aggregate. This process is repeated at different moisture contents (preferably near to the SSD condition). Once it appears that the paper towel is no longer picking up moisture from the aggregate, it is assumed that a surface dry condition has been reached and that the aggregate moisture content can be determined.

The cobalt chloride method (O’Neil & Smith 2001) also involves immersing the aggregate in water for 24 h after which the water is decanted and the surface of the aggregate is dried. At that time, a small amount of cobalt chloride powder is sprinkled on the surface of the aggregate. Cobalt chloride changes color in the presence of moisture from blue in the anhydrous (i.e., dry) form to pink when it reacts with water. This process is repeated at different moisture contents (preferably near the SSD condition). After a photo is taken, the cobalt chloride is removed from the surface of the aggregate and the aggregate is placed in the oven to determine the moisture content. When there is a higher moisture content, more water is on the surface of the aggregate and therefore more water can react with the cobalt chloride, resulting in a deeper red color. As the aggregate dries and the moisture content decreases a lower extent of reaction occurs resulting in the cobalt chloride appearing bluer.

The images of cobalt chloride on the surface of the aggregate were analyzed in image processing software (ImageJ©, freely available at http://rsbweb.nih.gov/ij/). The original RGB images were split into three separate images according to the red, green and blue color. The area of the cobalt chloride on the surface of the aggregate of the blue image was selected and the average hue of the cobalt chloride was determined.

Figure 1 shows the average hue of blue obtained from the image analysis as a function of the moisture content in the aggregate. The average hue will increase as the aggregate dries since unreacted (i.e., dry) cobalt chloride is blue and only the blue image was processed. An image
was also captured of cobalt chloride in the unreacted (i.e., dry) state to determine the upper bound of the hue of blue. The upper bound represents the theoretical maximum hue that could be reached. The aggregate begins to reach this value at low moisture contents. This is because no water is on the surface of the aggregate to react with the cobalt chloride. A lower bound was also determined by combining cobalt chloride with water and letting a complete reaction take place.

The results from the paper towel and standard cone methods are also shown along with the cobalt chloride method on Figure 1. The color change appears to begin to stabilize (which would indicate no water is on the surface) at approximately 11%. This is close to the 10.5% indicated by the standard cone method. It should be noted that some difference is observed between each method which can influence the mixture design. The impact of these differences will be presented later in this section.

![Figure 1: Average hue of blue at different moisture contents for LWA using the cobalt chloride method and comparison with the standard cone and towel paper methods. The average standard deviation for the cobalt measurements was approximately 5, and the average standard deviation of the moisture contents was 0.5%.](image)

The aforementioned methods rely on saturating a specimen for 24 h and then determining the disappearance of surface moisture for determining the absorption capacity of the LWA. It is important to note however that the further absorption of water by the lightweight aggregate takes place over time. Figure 2(a) shows the rate at which LWA absorbs water during the first 48 h starting from an oven-dry condition. This shows that while the rate of water absorbed during the first several hours is very high, the total absorption will continue to increase for several days, weeks, or months. As a result it is very important to know that any extra absorption during the time elapsed between mixing and set will be conditioned by the amount of time that the LWA was presoaked.

Figure 2(b) evaluates the effect of a change in the value of absorption assumed for mixture proportioning. This difference can be produced because of a miscalculation of the actual absorption or because of additional water absorption produced after mixing and before set. From Figure 2(b), one can see that a variation in the reported absorption value of ±2% (similar to the variation measured with the three test methods) will produce a change in the actual w/c in the range of ±0.01 (w/c between 0.29 and 0.31). In other words, if a LWA absorption of 10.5% is assumed, but the actual absorption is 8.5%, the mixture will have additional water resulting in a higher initial mixing w/c, because the LWA is pre-mixed with the total water as described earlier. This example is based on the Mixture 23.7% from Table 1, and assumes 10.5% of absorption for the LWA at 24 h.

Moisture desorption may be even more important than absorption capacity, because it will determine how much of that available water (absorption capacity) will actually participate in the hydration of the cement. Moisture desorption is an established technique for evaluating the effects of temperature and relative humidity on the moisture content of a material.
Figure 2. (a) Absorption of LWA over time (typical variability in the average of 3 samples is 0.1 %).
(b) Evaluation of the effect of a change in the absorption on the effective w/c for mixture 23.7 %

The desorption response was also measured for LWA after it was oven dried for 24 h ± 1 h, cooled, and placed in deionized water for 24 h ± 1 h prior to testing, to prewet the aggregate. The prewetted LWA was removed from water and “patted to SSD” using absorbent towels. A 70 mg to 100 mg sample was placed in a tared 180 mL quartz pan. The pan containing the sample was then suspended from the balance (± 0.001 mg accuracy) and placed in the relative humidity chamber to equilibrate at 23.0 ± 0.1°C and 98 ± 1% RH for up to 48 h or until the sample had achieved a stable mass (less than an 0.001 % mass change/15 minutes). After the sample equilibrated, the relative humidity in the chamber was changed in 1 % RH steps to 80 % RH, allowing the sample to equilibrate at the new humidity (less than an 0.001 % mass change/15 minutes or 12 h of exposure, unless noted otherwise). After equilibrating at 80 % RH the samples were dried to 0 % RH for up to 48 h or until the sample had achieved a stable mass.

Figure 3 shows the desorption response of LWA samples that were conditioned as mentioned in the previous paragraph. This LWA appears to be a good aggregate for use in internal curing, since a large volume of the water leaves the aggregate at high (i.e., greater than 90 % or 95 %) relative humidity, exactly when this water is most needed by the hydrating cement paste.

After the absorption-desorption behavior of the LWA has been accurately characterized, it is possible to study the effect of using LWA as internal curing agents. In this research, two test methods will be used to assess the effect of LWA on performance: sorption or water absorption (ASTM 2004), and degree of hydration by measuring the heat of the reaction.

Figure 3. Typical Desorption Response for LWA (typical variability in the average of 2 samples is 0.2 %).
5 EVALUATION OF HYDRATION AND DENSIFICATION OF MICROSTRUCTURE

5.1 Heat of hydration

Internal curing supplies additional water that can increase hydration of the cement and densify the microstructure at the surface of the lightweight aggregate. To measure the potential increase in hydration, an isothermal calorimeter was used. The cumulative heat of hydration was measured during the first seven days after mixing for three mortar mixtures with a \( w/c \) of 0.30 and three volumes of LWA 0 %, 11.0 % and 23.7 %. Approximately 20 g of externally mixed mortar were placed into each vial, with two replicates for each mixture.

Figure 4 shows the measured heat of hydration normalized by the theoretical maximum heat of hydration. This maximum theoretical value (476 J/g of cement) was calculated using the heat of hydration of the cement compounds (measured in cement) reported by Gartner et al. (Bensted, J and P. Barnes, 2002). The mixtures containing the pre-wetted LWA show an increase in heat that can be related to an increase in the degree of hydration. The effect of internal curing can be seen even at early ages due to the supply of additional water from the LWA. A similar increase in heat released at 7 d has been observed in \( w/c = 0.40 \) mortars prepared with internal curing (Bentz et al, 1999).

Mixtures 23.7 % and 11.0 % show an increase of 7 % and 6 % respectively on the heat of hydration at eight days compared with the plain mortar (M-0.30). It can be seen that the addition of LWA slightly increases the degree of hydration, but doubling the amount of LWA (from 11.0 % to 23.7 %) did not have a significant impact on the overall hydration of the mixture during the first 8 d.

![Normalized heat of hydration for \( w/c = 0.30 \) mortars](image)

Figure 4: Normalized heat of hydration for \( w/c = 0.30 \) mortars (typical variability at 8 days in the average of 2 samples is 0.2 J/g of cement)

5.2 Sorptivity

The effect of aggregate interfaces and additional hydration was further evaluated by performing the sorption test as specified in ASTM C1585 (ASTM, 2004) on samples containing LWA and plain mortars used as references. Three 100 mm × 200 mm cylinders were cast for each mixture. After one day of curing, the samples were demolded and three 50 mm ± 2 mm thick samples were cut from the central portion of each cylinder with a masonry saw, using water as a lubricant. The samples were sealed in two plastic bags until they reached an age of 28 d. After curing, the samples were prepared and tested in accordance with ASTM C1585-04.

Figure 5 show partial results of the sorption tests performed in this research. Additional information about these results can be found in Henkensiefken et al. (2009b). Figure 5(a) shows the relationship between the amount of absorbed water at 8 d and the \( w/c \) for samples first cured for 28 d. Because of the continued hydration of the LWA mixtures, they exhibit behavior equivalent to that of a conventional mortar with a lower \( w/c \). A “mortar equivalent \( w/c \)” (i.e., the \( w/c \) of a mortar sample that would exhibit a similar absorption to the absorption in the LWA mixtures) is shown in Figure 5(a). The 11.0 % LWA mortar with \( w/c = 0.30 \) has a performance
similar to a mortar with a w/c of 0.28, while the 23.7 % LWA mixture exhibits a sorption performance equivalent to a mortar with w/c of 0.23.

Figure 5(b) shows the same data as Figure 6(a), but now is used to determine a “cement paste equivalent w/c”. The 55/0.30 mixture has a performance similar to a paste sample with w/c of 0.37. The 11.0 % LWA mortar has a performance similar to a paste with a w/c of 0.35, while the 23.7 % LWA mixture exhibits a performance equivalent to a paste with w/c of 0.30. In general, a conventional mortar of a specific w/c such as 0.30 exhibits a higher absorption per unit volume of paste than an equivalent cement paste, suggesting the porous and well connected ITZs surrounding each NWA are contributing to increased sorption relative to a plain paste where no such ITZs are present.

Different from what was found with the heat of hydration, a higher amount of LWA was required to produce significant effects on the water absorption results. This suggests that the reduction in the overall water absorption may be related to a reduction in the porosity around the aggregates (ITZ) and a depercolation of the ITZ system, more than with an increase in the overall degree of hydration of the cement.

6 CONCLUSIONS

This paper examines the difficulties of an accurate determination of LWA absorption and the effect on increasing durability when LWA is properly used. Specifically, this paper has shown that:

- The available test methods to evaluate the absorption capacity of LWA (standard cone test, provisional cone test, paper towel test and cobalt test) can obtain values that vary in the order of 2 % - 3 % absolute absorption.
- Eventual additional absorption of water by LWA after casting is not considerable when the LWA is first pre-soaked for 24h. This extra absorption will have a negligible influence on the effective w/c of the mixtures.
- The addition of LWA as an internal curing agent increases the degree of hydration, producing a denser microstructure. The increased density of the microstructure results in less water absorption and reduced ionic (electrical) transport.
- From a sorptivity perspective, the w/c = 0.3 mixture with 23.7 % LWA performs better than the conventional mortar mixture with a w/c = 0.25.
- Comparing results of heat of hydration and sorption, it can be deduced that this densification occurs preferentially around the aggregate interfaces.
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REFERENCES