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by

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## MEASUREMENT OF WATER TRANSPORT FROM SATURATED PUMICE AGGREGATES TO HARDENING CEMENT PASTE

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### ABSTRACT

In this study about internal curing of High Performance Concrete, X-ray absorption showed that considerable transport of water from saturated lightweight aggregates (pumice) to hydrating cement paste [water/cement (w/c) ratio 0.3] took place in the first days after casting and covered a distance of at least 4 mm. As a consequence, the amount of water released by the lightweight aggregates, rather than the spatial distribution of the aggregates, is in this case the crucial factor to avoid early-age self-desiccation shrinkage.

### INTRODUCTION

High strength cementitious materials are characterized by superior properties in the hardened state. Yet, their application encounters some difficulties, in particular due to sensitivity to early-age cracking, which is associated with self-desiccation and autogenous shrinkage (1). Conventional curing techniques are not always effective in eliminating cracking, since the water migration into the concrete is limited by the tightness of the cement paste (2).

An effective strategy to overcome this problem is the use of pre-soaked lightweight aggregates (LWA) as internal water reservoirs. Several investigators have explored this concept in the last 10 years (3-5). These studies investigated the effects on the reduction of autogenous shrinkage of the replacement level of normal weight coarse aggregates by saturated LWA and of the degree of water saturation of the LWA.

Other studies focused on the mechanisms of internal curing, pointing out that, in order to avoid self-desiccation, the amount of entrained water should equal the volume of chemical shrinkage of the cement paste (6). Moreover, the spatial distribution of the 'water reservoirs' in the mixture is considered of primary importance in the internal curing process. The distance of the saturated LWA from the point in the cement paste where the relative humidity drop takes place determines the efficiency of the internal curing. The maximum transport distance of water, as a consequence of the depercolation of the pores in a low w/c ratio paste, was estimated as few hundreds of micrometers at later ages (2). With water-reservoirs well distributed within the matrix, shorter distances have to be covered and the efficiency of the internal-curing process is increased. According to these considerations, a novel concept in internal curing is based on dispersing very small, saturated LWA throughout the concrete, which will serve as tiny reservoirs with sufficient

water in them to compensate for self-desiccation. The spacing between the particles will be sufficiently small so that the water they supply will not have to diffuse/percolate over a large distance to counteract self-desiccation. The reservoir of water in the LWA could therefore be kept to a minimum, thus economizing on the content and porosity of the LWA (7-9). In these conditions, determination of the distance the water in the LWA can cover in the hydrating cement paste becomes a factor of paramount importance to improve the effectiveness of internal curing.

In this study, the X-ray profile of a sandwich specimen composed of saturated pumice and fresh cement paste was measured as a function of hydration time with the GNI X-ray System<sup>1)</sup> (10). Changes in the X-ray counts measured by a detector are related to changes in density of the medium through which the X-rays are traveling (11), higher counts being measured for lower densities. In this case, the moisture transport from the pumice to the hardening cement paste should result in an increase of counts in the pumice, which is losing moisture, and a decrease of counts in the cement paste. In past research, the X-ray system had been used to measure drying profiles of cement paste at early ages (12,13). Also transport of water from high to low w/c ratio pastes was detected (14). In these studies, water was observed to easily migrate over distances of 5 mm and more during the drying of fresh cement paste (12-14). Moreover, transport of water from super-absorbent polymers to cement paste was measured (15).

## MATERIALS

### Pumice

Crushed pumice sand from the island of Yali, Greece, was used in the experiments. The specific gravity was 1200 kg/m<sup>3</sup>. Water absorption by vacuum impregnation was mass fraction of about 35 %. Details about absorption-desorption and pore structure of the pumice are provided in (16). A low-magnification scanning electron microscope picture of the surface of a pumice particle is provided in Figure 1, left, which shows the rough surface of the grain and some pores with diameter around 100 μm. A higher-magnification picture of the inner pore structure of the aggregate is provided in Figure 1, right. In this picture pores ranging from hundreds of micrometers to a few micrometers are visible. The pumice appears to be highly porous, with pores distributed over a wide range of sizes.

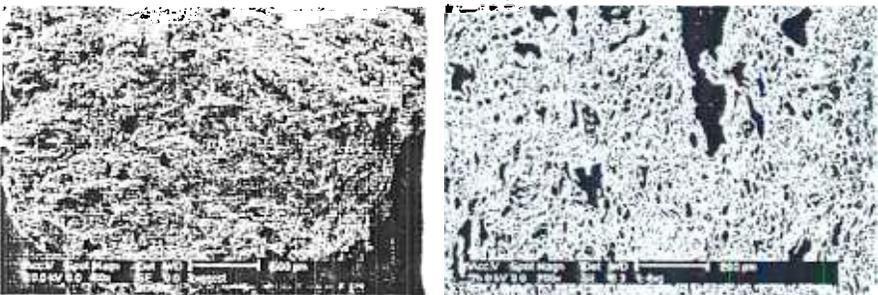


Figure 1. Scanning electron microscope pictures of pumice aggregates.

1) Certain commercial equipment is identified in this report to specify the experimental procedure. In no case does such identification imply endorsement by the National Institute of Standards and Technology, nor does it indicate that the equipment is necessarily the best available for the purpose.

**Cement paste**

The cement paste used was made with Portland cement, CCRL Cement 135 (17), and had a w/c ratio of 0.3. The Blaine fineness of the cement was 394 m<sup>2</sup>/kg. For Cement 135, a large amount of experimental and numerical simulation data about hydration was available (17,18).

**METHODS**

**X-ray absorption measurements**

Large flat pumice grains were selected from the largest fraction of the aggregate (> 4.75 mm). To obtain a flat and smooth interface with the paste, the aggregates were polished with sandpaper to obtain prisms, 10 mm x 4 mm x 2 mm. The LWA were cleaned by ultrasound in ultra-pure water for 1 min to remove any dust produced by the polishing. Aggregates were then vacuum dried and weighed. Subsequently, they were evacuated under high vacuum and impregnated with distilled water for about 3 h. The aggregates were left in the water overnight. The surface of the aggregates was then dried with an air stream and the saturated-surface-dry mass was measured. The LWA contained about 35 % water by mass fraction.

The sample holder used in the test consisted of a disposable 10 mm-pathlength semi-micro cuvette. The cuvette was made of polymethyl methacrylate, with an internal crosssection 4 mm x 10 mm and wall thickness of 1 mm. A thin slice of polished granite stone (about 10 mm x 4 mm x 3 mm) was inserted first into the cuvette, providing a support for the pumice that was inserted above. A tiny droplet of epoxy glue ensured adhesion between the granite and the pumice. The cement paste was mixed by hand in a sealed plastic bag for about 3 min. It was then poured into the cuvette on top of the pumice. During pouring, the cuvette was kept vertical. About 180 mm<sup>3</sup> of paste were poured, corresponding to a thickness of 4.5 mm above the LWA. Calculations showed that the water absorbed by the pumice grain was more than sufficient to fill the voids created by chemical shrinkage of the cement paste (16). A second slice of granite was inserted on top of the paste. A rubber cylinder was then pushed into the cuvette to ensure good sealing and the cuvette was closed with a polyethylene cap and sealed with epoxy glue. A schematic view of the whole specimen is shown in Figure 2. At this point the cuvette was turned horizontally and inserted into the X-ray chamber, kept at 25±1 °C, with the 4 mm side in the direction of the X-ray beam. The first reading started immediately and consisted of scanning the layered specimen from end to end in 0.2 mm steps. The measured accuracy of the positioning of the X-ray beam was 0.04 mm. The collimator of the detector had a circular opening with a diameter of 0.16 mm. Assuming a Poisson process, the relative standard uncertainty in the total counts should be on the order of 300 counts or 0.4%, for a total counts value of 70,000 (12,14).

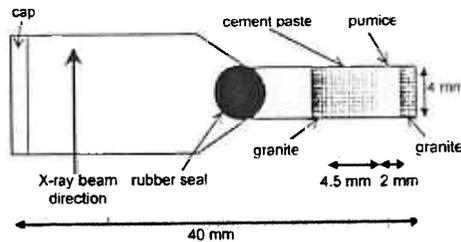


Figure 2. Schematic view of the specimen used in the X-ray absorption experiment.

### Chemical shrinkage measurements

About 5 g of freshly mixed cement paste were cast in the bottom of a small glass jar, with diameter 25 mm and height 60 mm. The thickness of the cement paste sample was about 5 mm. After the cement paste was covered with 1 mL of water, the jar was filled with hydraulic oil. The jar was sealed with a rubber stopper encasing a pipette graduated in 10  $\mu\text{L}$  increments and placed in a constant-temperature water bath at 25 °C. The oil level within the pipette was measured to the nearest 2.5  $\mu\text{L}$  over time. The chemical shrinkage per gram of initial cement was determined by normalizing the change in volume to the mass of solids in the sample. For each measurement, two specimens were tested. The maximum expanded uncertainty (18) in the calculated chemical shrinkage has been previously estimated (19) to be 0.001 g water/(g cement), assuming a coverage factor of 2 (A).

### Non-evaporable water measurements

The non-evaporable water content,  $W_n$ , is defined as the mass loss per gram of original cement, measured between the temperatures of 105 °C and 1000 °C. From the non-evaporable water content, the degree of hydration can be estimated assuming a value for the non-evaporable water of a fully hydrated sample. This value can be calculated from the Bogue phase composition of the cement ( $C_3S$  56.5 %,  $C_2S$  14.3 %,  $C_3A$  5.9 %, and  $C_4AF$  6.6 %); in the present case a value of 0.235 g  $H_2O/g$  cement was used (18). The specimens were stored inside the X-ray chamber (25 $\pm$ 1 °C) to realize the same conditions as in the moisture transport samples. Both saturated and sealed samples were tested. After 8 h, 1 d, 3 d, 7 d, and 28 d, one sample of each curing condition was crushed with a pestle in a mortar. The powder was flushed with methanol twice to stop hydration. Two crucibles were partially filled with the content of each sample and dried overnight in the oven at 105 °C. The crucibles were subsequently weighed and fired in the furnace at 1000 °C for about 3 h. The difference between the two masses, compensated for the loss on ignition of the dry cement powder, represented the non-evaporable water content of the sample.

### Numerical simulation of cement hydration

Hydration of the cement paste was simulated with the program CEMHYD3D. For details of the modeling, see (18). Chemical shrinkage and degree of hydration in saturated and in sealed curing conditions at 25 °C were calculated as a function of curing age. Curing in saturated conditions in CEMHYD3D is realized by guaranteeing free availability to water for hydration throughout the simulation. In the experiments, however, depercolation of the capillary pores in the low w/c paste after a few days hydration will limit access of the water: some self-desiccation will take place and further hydration will be hampered. After depercolation of the capillary porosity, the measured non-evaporable water content in the "saturated" samples will therefore be lower than in the ideal case of perfect saturation, but higher than in the case of sealed hydration.

## RESULTS

### X-ray absorption

The X-ray counts through the specimen measured immediately after casting and after 10 d hydration are shown in Figure 3. In the figure, the different materials that compose the layered specimen are also indicated. In Figure 4, the differential counts normalized to the initial counts

(after 1 h hydration) in each position along the profile are shown as a function of age. Figure 5 shows the differential counts normalized to initial counts, summed on the cement paste; on the LWA, and on the interface.

The presence of a smooth transition between the high counts in the LWA and the low counts in the paste (Figure 3) is due to:

- 1) The presence of an interface at the rim of the pumice grain.
- 2) The shape of the pumice grain, which is not perfectly prismatic.
- 3) The imperfect alignment between the pumice and the cuvette and the cuvette and the X-ray beam (Figure 2).
- 4) The width of the X-ray beam, whose diameter is 0.16 mm.

This region has been labeled *interface* in Figures 3-5. The distances from the interface in Figures 3 and 4 are positive in the direction of the pumice and negative in the direction of the paste.

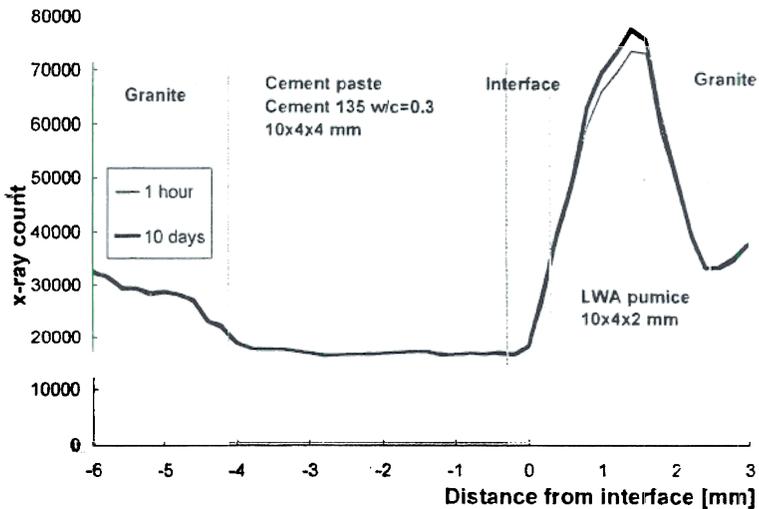


Figure 3. Initial and final X-ray counts profiles of the layered sample.

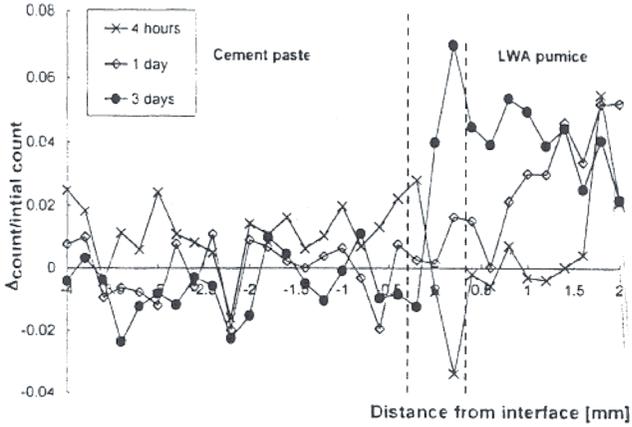


Figure 4. Difference in counts normalized to initial counts after 1 h hydration in cement paste and LWA at different ages.

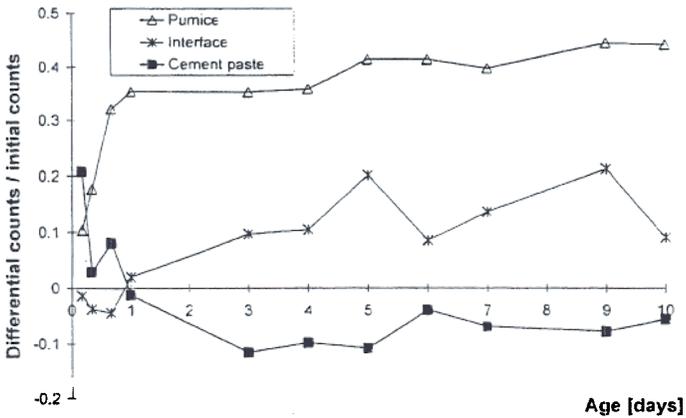


Figure 5. Difference in counts normalized to initial counts after 1 h hydration in cement paste, LWA, and interface as a function of age.

**Chemical shrinkage and non-evaporable water content**

Measured and simulated chemical shrinkage curves are shown in Figure 6. The deviation between the two curves after about 100 h may be due to depercolation of the capillary pores. If

the thickness of the chemical shrinkage sample is reduced, curves that are closer to the numerical simulation are obtained (21).

In Figure 7 the measured and simulated development of the degree of hydration is shown, both in sealed and in saturated conditions. The simulated curve for saturated conditions corresponds to ideal conditions of complete saturation, whereas depercolation of the capillary pores in the measured sample may have reduced the penetration of water into the sample at later ages and limited the hydration.

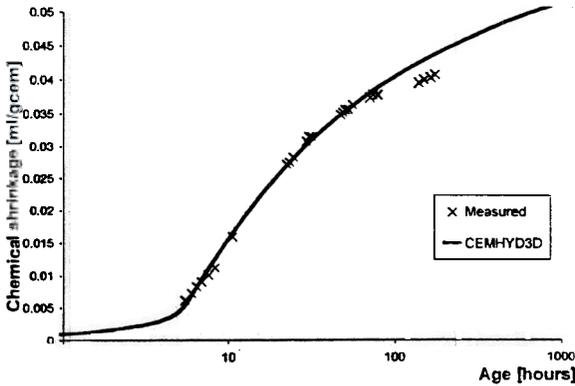


Figure 6. Measured and simulated (CEMHYD3D) chemical shrinkage of cement paste in saturated conditions as a function of age.

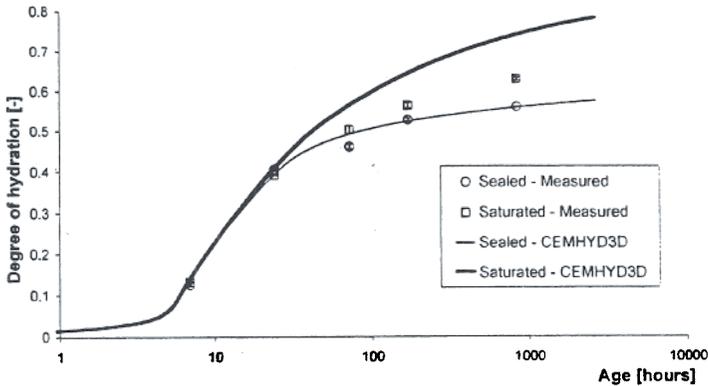


Figure 7. Measured and simulated (CEMHYD3D) degree of hydration of cement as a function of age based on non-evaporable water. Standard deviation bars are also shown in the graph.

DISCUSSION

The X-ray counts in the paste increase at 4 h almost at any point, decrease in the following readings and stabilize after 7 d (Figure 5). The first rise may be due to settlement of the paste between casting and the 4 h reading, as has been observed previously (12,14). The subsequent decrease of counts, corresponding to an increase in density, is probably due to absorption of water from the LWA.

The counts in the LWA in the first hours increase at the right end and decrease at the left end (Figure 4), possibly indicating a moisture transport within the thickness of the pumice. Afterwards, the counts on the whole LWA increase and then become almost stable after 3 d hydration. The interface region sees a decrease in counts in the first hours (Figures 4 and 5) and then a sudden increase. The oscillations in counts in the following days might be due to measurement error. In fact, the sharp gradient in counts in this region (Figure 3) amplifies the effect of the uncertainty in the positioning of the x-ray beam, which is about 0.04 mm.

In synthesis, the behavior observed in the X-ray absorption test corresponds to settlement in the paste in the first 4 h, which is the dormant period of the hydration of the paste (18). Once setting takes place, pores are emptied in the cement paste and water is pulled out of the LWA, passing through the interface first. Water is detected while it is passing from the right edge of the pumice to the left, through the interface and then into the paste. From 1 d, the counts in the interface are decreasing, and then by 3 d the whole transport process is almost over.

The chemical shrinkage in the paste is the driving force for the moisture transport. As progressively smaller pores are emptied in the cement paste (1), a gradient of relative humidity forms between the saturated pumice grain and the hardening paste, which pulls water out of the LWA. On the other hand, the evolution in time of the counts difference between the LWA and the cement paste represents a measure of the water transported. These two quantities are plotted together in Figure 8, where the chemical shrinkage was zeroed at 1 h to correspond to the initial X-rays measurement.

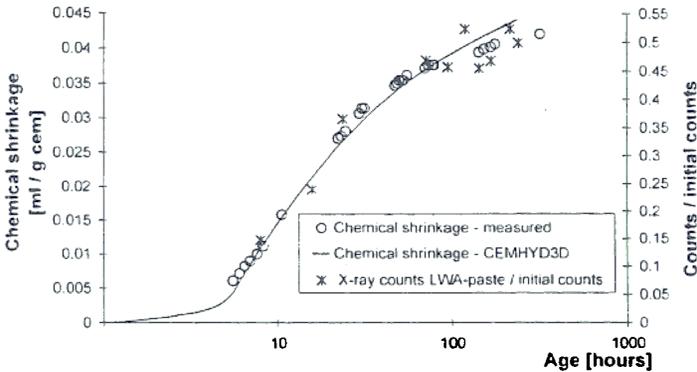


Figure 8. Counts difference as a function of age.

Figure 8 shows that the difference in change of counts between the pumice and the cement paste follows the same evolution as the chemical shrinkage in the paste. This fact confirms the assumption that the chemical shrinkage is the driving force pulling water out of the LWA. Since the counts are changing at all points in the cement paste layer (Figs. 4 & 5), the transport of water seems to be effective throughout the whole width of the cement paste, about 4 mm, in agreement with measurements of water movement during the drying of fresh cement paste (12,14).

Free transport of water through the cement paste may occur until depercolation of the capillary pores takes place, at about 4 d of age in this case. In fact, Figure 6 shows that at 100 h the simulated and measured curves for chemical shrinkage diverge, indicating the occurrence of depercolation. Most of the chemical shrinkage and the water transport from the pumice grain to the paste occurs in the first 4-5 d, before depercolation of capillary porosity, as evident in Figs. 5 and 6. Therefore, the transport of the internal curing water in the studied composite is not hampered by depercolation of capillary porosity and is effective on the millimeters scale.

The X-ray measurements confirm earlier results obtained in (16) with ink-impregnated expanded clay aggregates. Other researchers have reached the same conclusions observing the shrinkage reduction in concrete containing saturated pumice (22): transport distances of water up to several mm were calculated in concrete with w/c ratios 0.33 and 0.25. If the water transport is effective until few mm from the surface of the LWA, relatively coarse LWA particles might be also efficient for internal curing. Experimental evidence (4,16) supports this consideration: gravel-size LWA eliminated autogenous shrinkage in concrete with w/c ratio 0.37 and 5 % mass fraction silica fume addition.

The distance of water penetration into a hardening cement paste depends on its permeability and therefore is strongly influenced by the w/c ratio, by the cement fineness, and by the addition of silica fume. Moreover, depercolation is a gradual phenomenon and the transport distance of water will be reduced gradually, as paths through capillary pores are closed by hydration products. In pastes with very low w/c ratio and silica fume addition, depercolation of the capillary porosity may occur very early, so that ongoing hydration of cement and the pozzolanic reaction of silica-fume may still cause significant self-desiccation in the depercolated paste. In that case, the effective distance of water penetration from the rim of the LWA might be significantly reduced, perhaps to the 100  $\mu\text{m}$  to 200  $\mu\text{m}$  indicated in (2). At the same time, the phenomenon of depercolation requires further research.

## CONCLUSIONS

In this study performed with X-ray absorption, it was found that the transport of water from a saturated pumice aggregate to a hydrating cement paste (w/c ratio 0.3) followed the development of the chemical shrinkage of the paste during the first week of hydration. Moreover, the changes of X-rays counts in the specimen indicated a water penetration of about 4 mm from the rim of the LWA in the first days of hydration. This is in accordance with considerations about depercolation of capillary porosity in the cement paste, which should occur no earlier than 4 d in the present case. Before depercolation, water transport in the cement paste can take place over distances of at least several mm. As a consequence, for the cement paste studied, supplying a sufficient quantity of entrained water for internal curing in the first days of hydration, when most of chemical shrinkage occurs, is more important than having the water reservoirs extremely well-dispersed in the paste.

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