

# Effect of Relative Humidity on Expansion and Microstructure of Heat-Cured Mortars

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## 1. INTRODUCTION

The research described in this paper follows broader studies aimed at investigating Delayed Ettringite Formation (DEF). The key role played by moisture exposure on the DEF phenomenon has been acknowledged since concrete expansion related to DEF became a matter of interest to investigators. However, little work has been done in elucidating the effect of varying humidity on possible DEF-related expansion of concrete under field conditions.

The work reported here is on the effect of moisture exposure on expansion of heat-cured mortar bars using saturated aqueous salt solutions to achieve constant relative humidity conditions. Storage conditions also included storage under water. The cement utilized in this research was used in previous research [1]. In the previous study mortars made with several cements exhibited a range of expansions after high-temperature curing. Cements from the same sources were also included in a parallel research study investigating the chemical path and mechanism of DEF [2].

Long-term storage conditions for samples studied were under distilled water, and above water at relative humidity percentages of 100, 97, 92, 90, 84, 80, and 75. Monitoring of RH and temperature was automated using humidity/temperature probes connected to a computer. Testing performed included measurement of weight and length changes at periodic intervals, chemical analysis by X-ray fluorescence (XRF), thermogravimetric analysis (TGA) techniques, and mineralogical analysis by X-ray diffraction (XRD). Microstructure characterization of mortars was also done by optical microscopy, scanning electron microscopy (SEM) and energy dispersive X-Ray spectroscopy (EDX) analyses [3]. Results of weight and length changes are presented in this paper.

## 2. EXPERIMENTAL METHODS

### 2.1 Mortar Bar Preparation

In a previous series of experiments the cement used had showed large expansion upon curing at 90°C [1]. The selected sample (designated as

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C09-III) met ASTM C 150 Type III specifications, and had a C<sub>3</sub>A content of 10% by mass, an SO<sub>3</sub> content of 4.5% by mass, and a specific surface area (Blaine fineness) of 531 m<sup>2</sup>/kg. In this previous study [1] the form of sulfate in the cement was characterized by thermal analysis. Gypsum, hemihydrate and syngenite were quantified.

Mortar bars were fabricated using a sample of cement from the same source. Table 1 shows the composition of the sample used in this study. A total of 40 mortar bars were prepared in accordance with ASTM C 109. Water:cement:sand ratios were 0.485:1:2.75 by mass. The sand used was graded standard sand conforming to ASTM C 778. This sand (commonly known as Ottawa sand) has been previously shown to be inert with respect to alkali-silica reaction.

Table 1. Chemical Oxide Analysis of Cement Used in Mortar Mixes

Analyte	Weight %	Analyte	Weight %
SiO <sub>2</sub>	19.59	P <sub>2</sub> O <sub>5</sub>	0.15
Al <sub>2</sub> O <sub>3</sub>	5.52	Mn <sub>2</sub> O <sub>3</sub>	0.21
Fe <sub>2</sub> O <sub>3</sub>	2.47	SrO	0.08
CaO	62.94	Cr <sub>2</sub> O <sub>3</sub>	<0.01
MgO	2.11	ZnO	<0.01
SO <sub>3</sub>	3.96	L.O.I. (950°C)	1.03
Na <sub>2</sub> O	0.27	Total	99.47
K <sub>2</sub> O	0.85		
TiO <sub>2</sub>	0.29	Alkalies as Na <sub>2</sub> O	0.83

The mortar was mixed in commercial Hobart mixer in a total of 8 identical standard batches in order to obtain sufficient mortar to cast 5 bars for each batch. Mortar bars were 285 × 25 × 25 mm (11¼ × 1 × 1 in.). Once the high-temperature curing was completed, mortar bars were demolded, labelled, and marked for length readings. Initial lengths and saturated-surface-dry weight of the bars were measured at 24 hours after mixing and samples were subsequently stored at 23°C in the environments described in Section 2.2. Changes in length and weight of the bars were monitored at ages of 2, 3, 4 and 7 days, once a week through 8 weeks, and at 10 weeks and 12 weeks. Thereafter, measurements were scheduled every month through 4 years. Expansion was calculated as change in length.

## 2.2 Curing and Storage

Following preparation, all mortar bar sets were pre-cured for 4 hours at room temperature in a moist room. Then they were introduced into a steam chest equipped with programmable controls. The chamber

temperature was increased at 20°C/hr for 3.5 hr to a maximum temperature of 90°C. Maximum temperature was held for 10 hr, and then temperature was decreased at 20°C/hr for another 3.5 hr.

Different salt solutions were used to control the relative humidity conditions to which the samples were exposed during long-term storage. The relative humidity inside the storage containers was that obtained at room temperature. Air temperature inside the containers was monitored, as well as air temperature outside the containers in the storage room. Saturated salt solutions for control of relative humidity, RH, were prepared based on data reviewed by Young [4], work referenced by him [5, 6], and data from the International Critical Tables [7]. The following salts were used: NaCl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, KCl, BaCl<sub>2</sub>, KNO<sub>3</sub>, and K<sub>2</sub>SO<sub>4</sub> to give RH of 75.1%, 80.2%, 84.2%, 90.3%, 92.0%, and 97% respectively. These solutions were allowed to reach equilibrium with their vapor in a sealed container at room temperature. Controlled relative humidity environments were achieved in the range from 75% to 100%. Relative humidity of 100% was achieved using tap water. One mortar bar set was also stored immersed under deionized (DI) water.

Relative humidity was monitored inside the storage containers starting immediately after saturated mortar bars were placed inside. The delay in reaching constant relative humidity conditions in the air lasted for about 2 weeks. After reaching equilibrium conditions, relative humidity was very close to constant, as shown in Fig. 1.

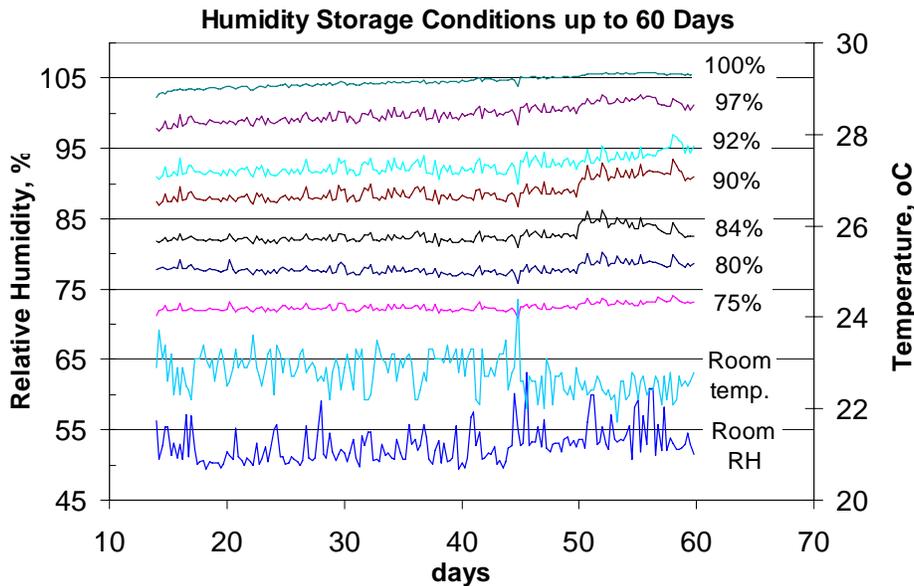


Figure 1. Storage conditions after stabilizing mortar-air humidity exchange. Recorded measurements over 100% RH are artifacts of the measurement.

However, a slight steady increase was observed for measurements of 90% RH and higher, which was expected according to the manufacturer of

the humidity probes. In addition, when measuring high humidity levels, the accuracy reported by the manufacturer is  $\pm 3\%$ . Additional effects of initial moisture exchange between the air and the mortars were reflected in the weight change of bars and will be discussed later.

Mortar bars in each set were labeled with their relative humidity storage condition, followed by a letter A, B, C, D, or E to designate its location in the container. Bars A, B, C, and D were used for length and weight measurements. Except for the mortar bars stored under water, the storage containers were filled with tap water (100% RH) or with saturated solution to a height of about 25 mm (1 in.). Mortar bars were placed on top of plastic grates to freely allow moisture movement, and also for supporting the bars horizontally parallel to the solution surface. Fig. 2 illustrates the arrangement of the bars in a side view of container No. 3. Fig. 3 is a top view of container storing bars immersed in water showing bar position and labeling. Bars were positioned and labeled the same way in all storage containers.

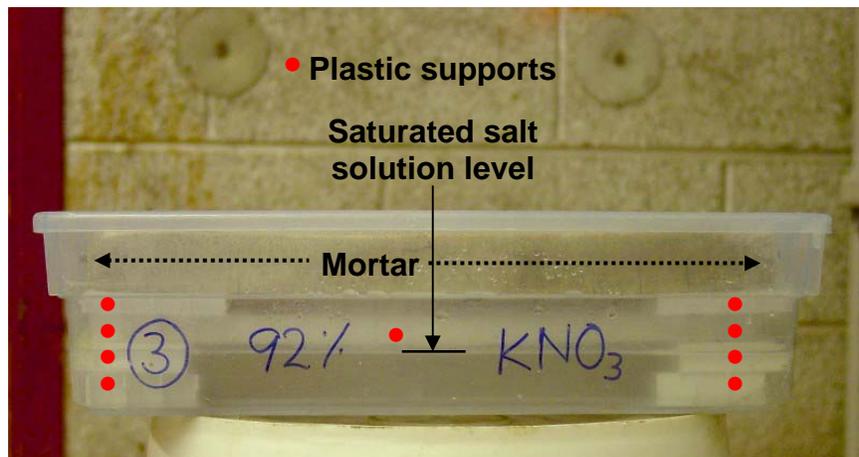


Figure 2. Side view of storage container No. 3 showing assembly of chamber

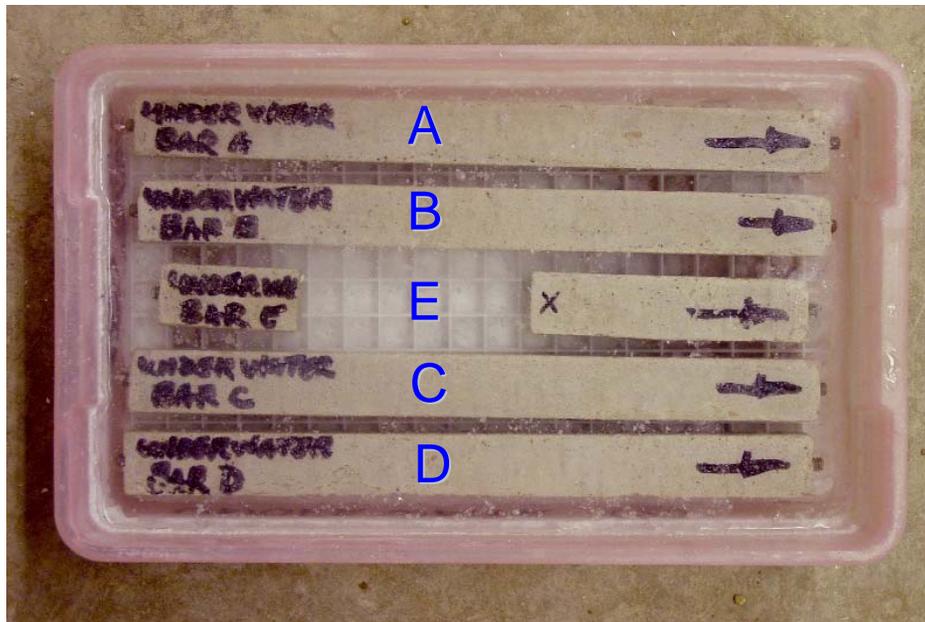


Figure 3. Set up, position, and labeling of mortar bars inside storage containers. Mortar bars stored under water expanded but without external cracking. Mortar bars stored in some RH-controlled atmosphere showed localized expansion resulting in cracking, see Fig. 4.

### 3. RESULTS AND DISCUSSION

#### 3.1 Expansion and Weight Change

Average expansion and weight change results are shown in Figs. 5 and 6 for all storage conditions. Expansion data shown includes measurements up to 1667 days (over 4.5 years). Expansion results for bars made with cement from the same source and stored immersed in lime-saturated water (ULSW) obtained in another research project [2] are included for comparison.

Expansion behavior of bars stored under water was substantially different from that of bars stored above water (compare Figs. 3 and 4). For the bars stored under water the expansion was uniform and the same for all specimens. For bars stored in air the expansion of individual specimens in a set was different and resulted in cracking concentrated at the ends of all bars, and in the center part of bars A and D located near the sides of the container (see Fig. 4). This cracking was not visible until about 500 days of age. The difference in behavior was also observed by the microscopical examination (thin sections and polished sections of cross sections) of the mortars [3]. In samples stored under water the microstructure was similar to that observed in other studies [2] with ettringite in gaps around sand grains and distributed in pores and microcracks. Samples stored in controlled RH only showed gap formation and ettringite in pores in the cracked areas of the samples only. In parts between cracks no gaps or

ettringite was observed in the paste of the mortar. These observations suggest internal expansion and cracking occurring in localized areas of the paste, rather than uniformly distributed throughout the specimen.



Figure 4. Mortar bars stored in 92% RH showing typical local expansion resulting in cracking.

The first mortar bar set to show expansion (Fig. 5), after about 50 days, was that stored under water. It reached a maximum rate at around 85 days, after which the rate remained the same until after around 200 days, when the expansion ceased at a maximum expansion of 0.3%.

The next set of bars to expand was the one stored above water at 100% RH. This set started to expand at a slower rate than the set stored under water, and its maximum rate of expansion was similar but occurred at around 185 days. The expansion continued at about the same rate, surpassing the maximum expansion level for the set stored under water at about 240 days. After about 640 days and 0.9% expansion the specimens were so deteriorated by cracking that the bar's lengths were not measurable.

The next set of mortar bars to expand was that stored above water at 97% RH. This set of bars showed an average expansion rate that reached its maximum rate at approx. 220 days. The expansion continued until it

surpassed the maximum level of expansion for the set stored under water (0.3%) at around 320 days. It continued to expand at a decreasing rate, reaching a level of 0.83% at around 670 days, after which measurements could not be made due to cracking and deterioration at the ends.

The final set to show expansion was the one stored at 92% RH. The maximum rate of expansion was reached at 400 days, and this rate remained high. Expansion surpasses the 0.3% mark at around 480 days. Bar ends deteriorated and lengths were not measurable any more after around 700 days, with an expansion of 0.9%.

No other set showed high rates of average expansion. The data plotted in Fig. 5 clearly shows that the sets stored at 90% RH and below did not exhibit expansion up to 1667 days. This observation indicates that a minimum level of exposure to moisture was required for expansion to start either because of insufficient amount of water available or because its activity is too low at these RH-levels for the reaction to occur (i.e. ettringite would not form at this low level of partial pressure of water). Alternatively the ettringite formation potential might have been exhausted and expansion not triggered.

The amount of available water is a function of RH and pore size distribution of the paste. The maximum pore size  $r_{RH}$  in which water can condensate is related to the RH by the Kelvin-Laplace equation. Substituting typical data for water in the original equation (assuming spherical pores) results in the following [8]:

$$RH = \exp(-1.0553/r_{RH}) \quad (\text{Eq. 1})$$

For a given RH level, pores up to  $r_{RH}$  are filled with water, and larger pores with water vapor. According to the model,  $r_{RH}$  corresponding to 75%, 90% and 92% RH are 3.7 nm, 10 nm and 12 nm respectively. Based on these considerations the available water amount is expected to increase by exposing the samples to increasing RH<sup>3</sup>. An experiment was conducted to test this idea and generate initial data: bars stored at 75% RH were transferred to 92% and 90% RH, while simultaneously some bars stored at 90% were also transferred to 92% RH. The results are shown and discussed in Section 3.2.

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<sup>3</sup> In terms of sorption isotherms this would be equivalent to move the system from the desorption isotherm to the absorption isotherm.

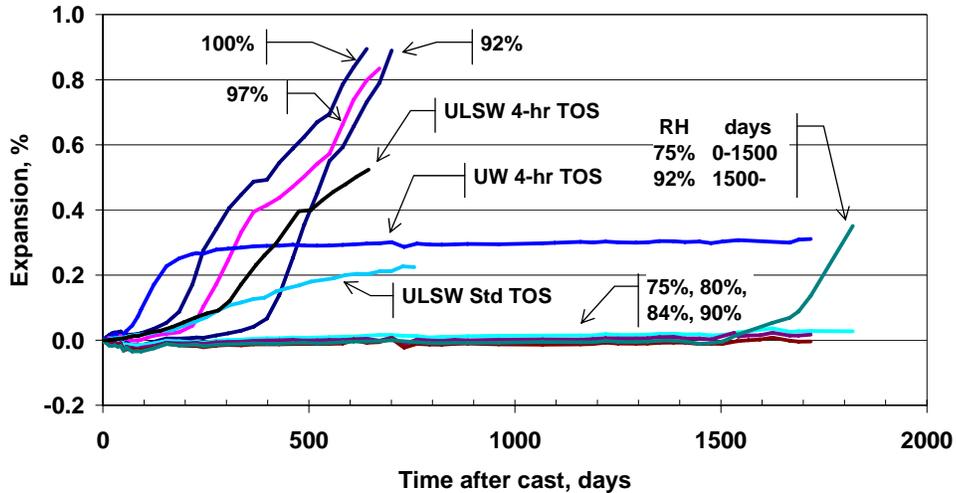


Figure 5. Average expansion of mortar bars stored at the indicated condition. UW= under water, ULSW= under lime saturated water, TOS= time of set.

The average weight change of the different sets is shown in Fig. 6. The weight curves fall in two groups. One group is mortar bars stored under water and in controlled humidity from 100% RH down to 97% RH. The other is bars stored at 92% RH and lower. For the first group the samples gain weight from the start of storage. The second group starts by decreasing weight and at later time gain weight at different rates. This behavior we interpret as follows: The RH of the pore system of which the solution is alkali and calcium hydroxide solution is generally accepted to be ~95%. Samples exposed to environments with RH >~95% will increase in weight by up-take of water consumed by continued hydration (degree of hydration after heat curing is about 75-80%) and ettringite formation. Samples exposed to RH <~95% will experience two competing processes: drying out until equilibrium with the surrounding RH is obtained and gaining weight by concurrent hydration and ettringite formation. Because of the limited water availability at low RH the hydration and ettringite formation are slowed down.

Carbonation also contributed to the weight gain and this may be the main contribution at late ages for the samples at low RH. XRD and TGA [3] identified  $\text{CaCO}_3$ . The above mentioned microscopy of samples showed carbonation of the paste at the surface of the bars. At the time of measurement, in the expanding samples (100% RH) and non-expanding samples (90%, 84%, 80% and 75% RH) the amount of  $\text{CaCO}_3$  was of the same order, indicating the carbonation of all samples were similar. In samples (all E-end samples, see Fig. 3) taken at the age of 1295 days the  $\text{CaCO}_3$  determined by TGA was 3.3 to 4.1% in the samples at low RH and ~2% in the sample from 100% RH.

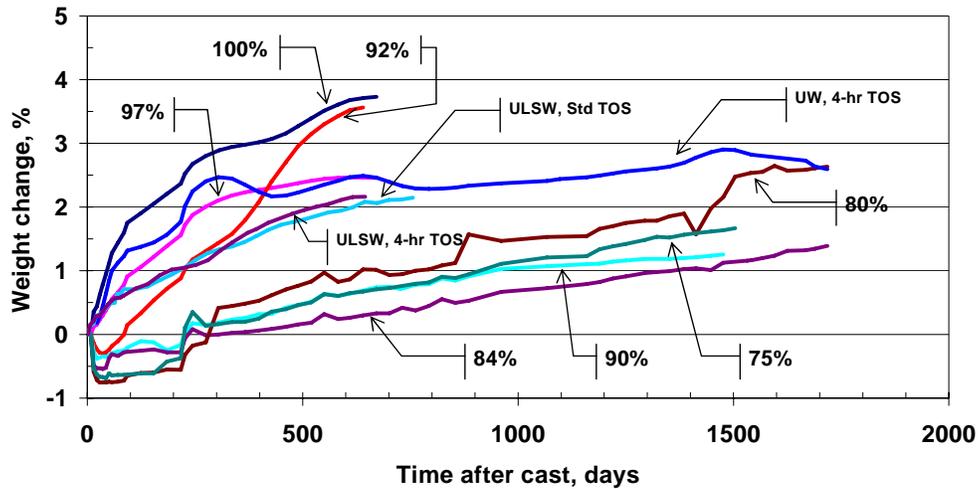
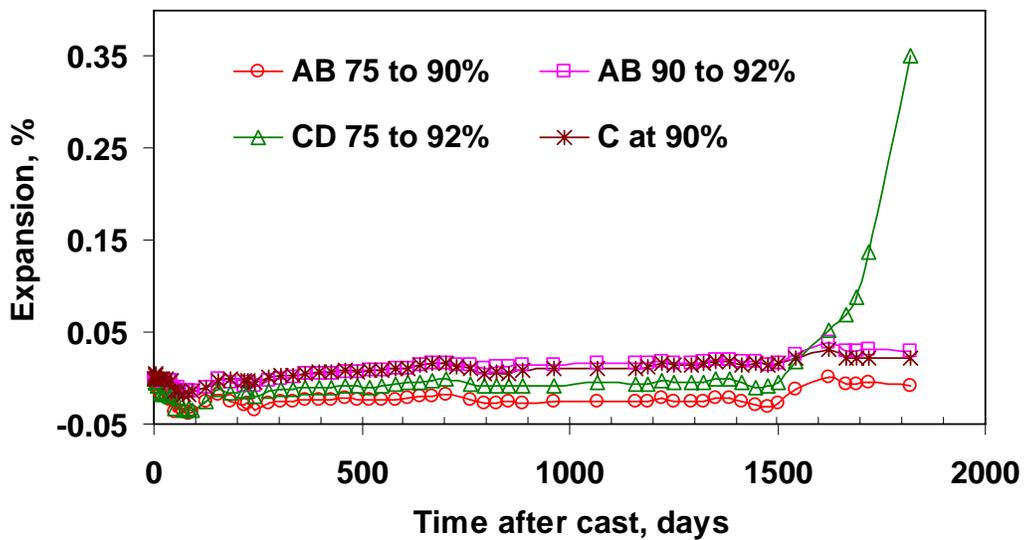


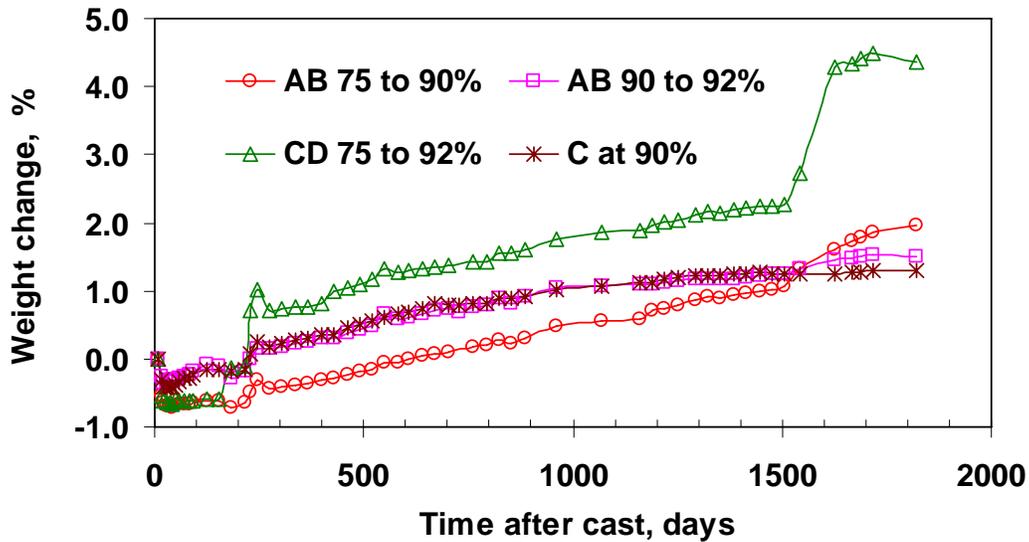
Figure 6. Average weight change of mortar bars stored at the indicated condition. UW= under water, ULSW= under lime saturated water, TOS= time of set.

### 3.2 Expansion and Weight Change after Exposure to Higher Humidity

After 1500 days storage bars A and B from the set stored at 75% RH were moved to 90% RH storage, and bars C and D stored at 75% RH were put into 92% RH storage. At the same time, bars A and B from the set stored at 90% RH were transferred into the 92% RH storage, and bar C stored at 90% RH was left in its original container. Figs. 7a and 7b below show the expansion and weight change results obtained for the transferred bars.



(a)



(b)

Figure 7. (a) Average expansion, and (b) average weight change, of combination of bars A, B, C, and D exposed to 75% and 90% RH for 1500 days, and subsequently exposed to higher RH after that period of time. The constant weight gain at later age up to 1500 days is mainly due to carbonation.

The most noticeable changes are observed for mortar bars stored at 75% RH and moved to 92% RH, where the average length change of bars C and D increases from just around zero to around 0.35% (see Fig. 7a). This expansion rate is similar to those obtained at the beginning of the experiment (Fig. 5). The average weight increases up to about 4.5% from 2.5% after some 100 days, and then stays unchanged for the remaining 200 days (see Fig. 7b).

In the case of bars transferred from 75% to 90% RH (bars A and B), expansion changes are small and considering measurement error may not be significant. This provides more evidence of a likely “threshold level” of moisture to trigger DEF-related expansion. However, as can be seen in Fig. 7b, average weight changes by about 1%.

The mortar bars transferred from 90% to 92% RH (bars A and B) show less indication of change. Average length change is small and maybe not significant. Average weight change is ~0.2%. Bar C shows no changes, as expected.

All samples had the same initial conditions after heat curing: pore size distribution, distribution of AFm in the nano-sized pores of C-S-H phase and hence the same potential for expansion due to DEF (after heat curing at 90°C no ettringite is observed [2]). Depending on water availability and

its activity ettringite will form at varying rates<sup>4</sup>. Ettringite formed in confinement may act as possible local pressure centers [9, 10, 2] resulting in expansion. A mechanism to relax this pressure is the Ostwald ripening [11] by which small crystals, e.g. ettringite, recrystallize into large crystals in available void space depending on amount of available water. If for some reason the formation and re-formation of ettringite is slow relative to the Ostwald ripening, expansion may not occur. This would be depending on connectivity of the pore system and internal moisture content, which in turn is a function of the RH the sample is exposed to.

Mortar exposed to 90% RH has had more moisture available compared to mortar exposed to 75% RH, and therefore may have re-formed more ettringite over the storage period of 1500 days, at a lower rate, though, than mortars exposed to higher RH. At the same time conditions provided for better ionic transport through the pore structure, allowing ettringite to re-crystallize and grow in available voids with the consequent stress relief. This is not inconsistent with the relative small weight gain observed (~1%) upon RH change, indicating small pore volume in the interval from 10 to 12 nm. In contrast, mortar bars exposed to 75% RH may not have re-formed as much ettringite and may still have latent potential for related expansion, as evidenced by the experiments. The observed weight changes for these samples indicate filling a relative large pore volume in the interval from 10 to 12 nm providing conditions conducive for ettringite formation.

#### 4. CONCLUSIONS

Heat-cured mortar bars stored at RH >~95% show weight gain immediately at the start of exposure. Mortars stored at RH <~95% show weight loss followed by a slow weight gain. This is interpreted as wetting and drying, respectively.

For the long-term storage of mortar bars exposed to all RH levels in the range from 75% to 100% (including under water storage), only exposure to 92% and higher resulted in cracking and expansion. Mortar bars stored in water expanded without cracking.

Even after 1500 days of exposure, subsequent exposure to higher levels of relative humidity provided the necessary conditions for triggering DEF-related expansion. This is observed in samples originally exposed to relatively low RH level (75%) that did not result in expansion, and which subsequently expanded when the RH increased from 75% to 92%.

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<sup>4</sup> The water is transport medium for the reactants as well as reactant in the formation of ettringite.

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