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X-ray absorption study of drying cement paste and mortar

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Abstract

X-ray absorption was used to observe water evaporation with hydration time in paste and mortar specimens, with the aim of studying the influence of water/cement (w/c) ratio, presence of aggregates, curing conditions on drying during early hydration. For the samples subjected to surface drying immediately after mixing, there exists a moisture gradient within the internal part of the specimen. However, obvious top-down drying only occurs within a small zone near the surface for early age cement pastes and mortars. The evaporation rate of water is very high in the first day after casting and is drastically reduced afterwards due to the formation of a microstructure that greatly improves specimens resistance to moisture loss. Mortars reveal a slightly lower evaporation rate since the aggregate increases the length of the transport route because of a larger tortuosity. However, the effect of sealed curing is much more important than the tortuosity effect of the aggregates.

Keywords: X-ray absorption; Cement paste; Mortar; Drying

1. Introduction

Water exerts very complicated influences on the microstructure development and the mechanical properties of cementitious materials. In a hydrating water/cement (w/c) system, water is present in roughly three different forms, viz. chemically bound water, physically bound water and free (capillary) water. In a parallel classification, a distinction has been made between evaporable and nonevaporable water. According to van Breugel [1], evaporable water includes gel water and capillary water that exist in pores with diameters larger than 0.001 μm. The borderline between evaporable and nonevaporable water is not a very distinct one.

The w/c ratio, curing conditions and cement composition are major factors affecting the water movement in cement and concrete. An increase of the w/c ratio has been reported to increase the nonevaporable water content [1]. The amount of physically bound or adsorbed water actually depends on the relative humidity in the pore system. As a rough guide value for the amount of physically bound water, a value of 15% of the weight of the anhydrous cement is generally adopted [1]. Assuming the 20 Å pores to be characteristic of the gel, it can be concluded that under normal curing conditions, the gel is completely saturated. This part of the physically bound water is, therefore, considered to be part of the gel and is not available for further hydration. Together with the amount of chemically bound water, i.e. 25% of the weight of anhydrous cement, the amount of water required for complete hydration would be about 40% of the weight of the cement. Free water is often equalized with evaporable water. This water is assumed to be available for further hydration of the cement.

In view of the complex existence and behavior of water in cement hydration, fundamental research is necessary to examine the spatial and temporal water distribution within cement and concrete. Recently, an X-ray environmental chamber has been constructed to examine building materials exposed to various drying regimes [2–4]. Relative humidity and air temperature can be conveniently and independently adjusted within the chamber. Based on the principle that X-ray absorption is proportional to the density of the material through which the X-rays are passing, this technique is used to monitor water movement during the early hydration of cement specimens in this preliminary study. A transmission beam from an X-ray source passes through the cement specimen to a detector that records the X-ray counts. Since the cement specimen is stored in a container, the total volume of the paste scarcely changes on hydration. Although complex chemical and physical reactions are

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associated with the process of cement hydration, accompanied by formation of hydration products and microstructural changes, the mass of the whole cement specimen should remain constant in such isolated condition unless a loss of evaporable water is caused by surface drying. Therefore, the X-ray counts–time curve allows determination of the global weight loss due to water evaporation, and the assessment of the drying profile.

2. Materials and experimental procedures

Details of the experimental set-up can be found in Refs. [2,3]. The X-ray source consists of an X-ray tube, requiring an energy level between 20 and 125 keV (75 keV in this study), with a maximum current of 0.5 mA. The filtered beam is collimated and the resultant 1-mm diameter beam passes through the specimen to be tested. A detector, with an NaI crystal, measures the photon count for each of the 256 discrete energy channels. The measured spectra for two ordinary fresh cement pastes with w/c of 0.3 and 0.45, respectively, are provided in Ref. [3]. The small peak at Channel 200 is proved to be caused by an internal cobalt source used for system calibration. Therefore, the sum of counts between Channels 1 and 160 was recorded and considered to be representative of the density of the cement paste. The resolution of the measuring position is on the order of 0.1 mm. The entire system is computer controlled.

Paste and mortar mixtures with two w/c ratios of 0.32 and 0.50, respectively, were cast in small vertical vials (a commercial equipment was chosen due to their generally low absorption of X-rays and their inherent stackability [3,4]), whereupon the X-ray count was measured at different heights. An ASTM Type I ordinary Portland cement was used. The mortar with w/c = 0.32 was composed of 529 kg/m^3 cement and 600 kg/m^3 sand. The mortar with w/c = 0.50 was composed of 414 kg/m^3 cement and 600 kg/m^3 sand. Maximum grain size of the sand amounted to 4 mm. The approximate internal dimensions of the vial are approximately, length = 5 mm (X-ray beam direction), width = 5 mm and height = 40 mm. A 5-s count time was used at each location to improve the signal-to-noise ratio [2,3]. The vial was placed on a holder in the X-ray chamber with controlled conditions of 23 °C and 40% RH. Each sample was measured at heights ranging from 15 to 55 mm, whereby 15 mm was at the bottom of the vial and 55 mm was on the level of the top surface of specimen. For each w/c ratio, one sample was exposed to drying immediately after casting ("a" sample), whereas the other one was capped during the first 26 h after casting and then exposed to drying ("b" sample). After specific periods of exposure, the X-ray system was used to scan vertically a distance of 40 mm ("measuring height" from 15 to 55 mm, with an interval of 5 mm) along the central vertical axis of each vial. Measurements were taken at 2, 5, 13, and then every 12 h until a total of 84 h.

3. Results and discussion

The global internal density of the cement specimen can be represented by the sum of X-ray counts at measuring height from 15 to 45 mm (corresponding to the internal part of the specimen). The global density for specimens exposed immediately after mixing to X-ray chamber environment ("a" group) is expected to decline gradually with the hydration time due to water loss. However, as a result of complex simultaneous reactions during the hydration process, the density profile of the specimen at different measuring heights (corresponding to different parts of the specimen, which are subjected to different local conditions) can be much more complicated. Thus, in addition to the determination of the global density evolution, it is as well necessary to investigate the moisture gradient within a single specimen.

3.1. Moisture gradient within the specimen

To provide insight into the moisture gradient in the cement specimen, the X-ray counts are plotted against hydration time for different measuring heights. The local density profile for a representative specimen—cement paste "a" of w/c 0.32 (denoted as "paste32a")—is shown in Fig. 1. Theoretically, a continuous trend can be expected in the drying process as reflected by proportionally rising X-ray counts with time for those locations affected by the drying process. Thus, globally a smooth gradient (apart from scatter) would arise over the active zone.

Fig. 1 reveals a quite complicated phenomenon, however. The curves show an increase within the first day, and remain relatively stable thereafter, with slight fluctuations. This density decline during the early hydration stage can be associated with a loss of water. After the first 26 h or so, due to setting and tightening of the microstructure, the moisture loss to the environment will reduce considerably.

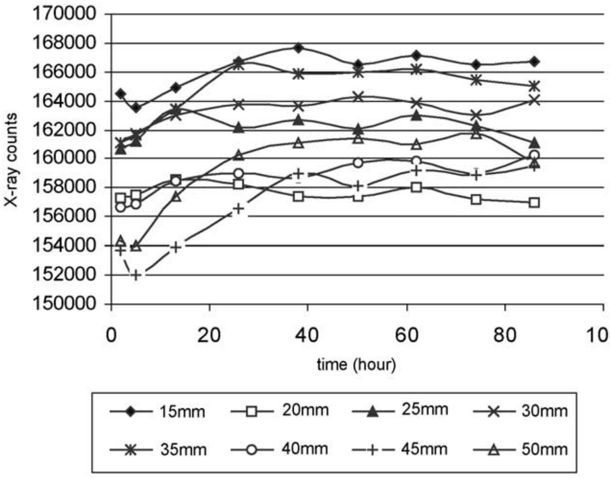


Fig. 1. Density evolution at different measuring heights for paste "a" with w/c = 0.32.

This will also release the under-pressure in the pores in the top layer and the resulting suction of water from the more remote parts of the specimen to the top. The curves, at heights of 45 and 50 mm, additionally reveal a small decrease of X-ray counts in the first 5 h before the steep increase sets in. This can be explained by the fact that the density decline due to water removal in this period is offset by the consolidation of the solid.

To give a clearer view of the density gradient, for pastes "a" and "b" of w/c 0.32 (denoted as "paste32a" and "paste32b," respectively), the X-ray counts are plotted over the height of the specimen in Fig. 2 as a function of maturity. The curves do not indicate a continuous decline in moisture content over the height of the specimen. According to the shape of the curves, the specimens can be divided into four parts, 15–20, 20–35, 35–50, 50–55 mm, respectively. At the bottom of the vial, corresponding to the measuring height of 15 mm, the X-ray counts are relatively high due to a less dense structure. A reasonable explanation is that at this location the so-called wall effect caused internal bleeding and a higher content of water-filled pores. This holds for both "paste32a" and "paste32b." The data reveal the water reduction to be quite uniform in the middle part of the specimen, especially for "paste32b." A gradual and clear increase of X-ray counts after hydration of 5 h is observed in the sections 20 to 35 mm of specimen "paste32a." This is the effect of water migration to the top section of the specimen, where pore pressure is reduced due to water evaporation. Although water migration reduces moisture in the central part, abundant water is still available for further hydration and hardening. As a result of continuous hardening, the density remains stable in the 20- to 35-mm sections, particularly for "paste32b." The effect of hydration time is much more pronounced for "paste32a" than for "paste32b." At the 35-mm level, after 5 h, water migration and water consumption by cement hydration result in a shortage of water and a decline in hardening rate, so the porosity increase should be larger than the hardening effect. This is demonstrated by the decrease in X-ray counts between 40- and 50-mm sections of the specimens, which indicates local density increase compared to the middle part of the specimen.

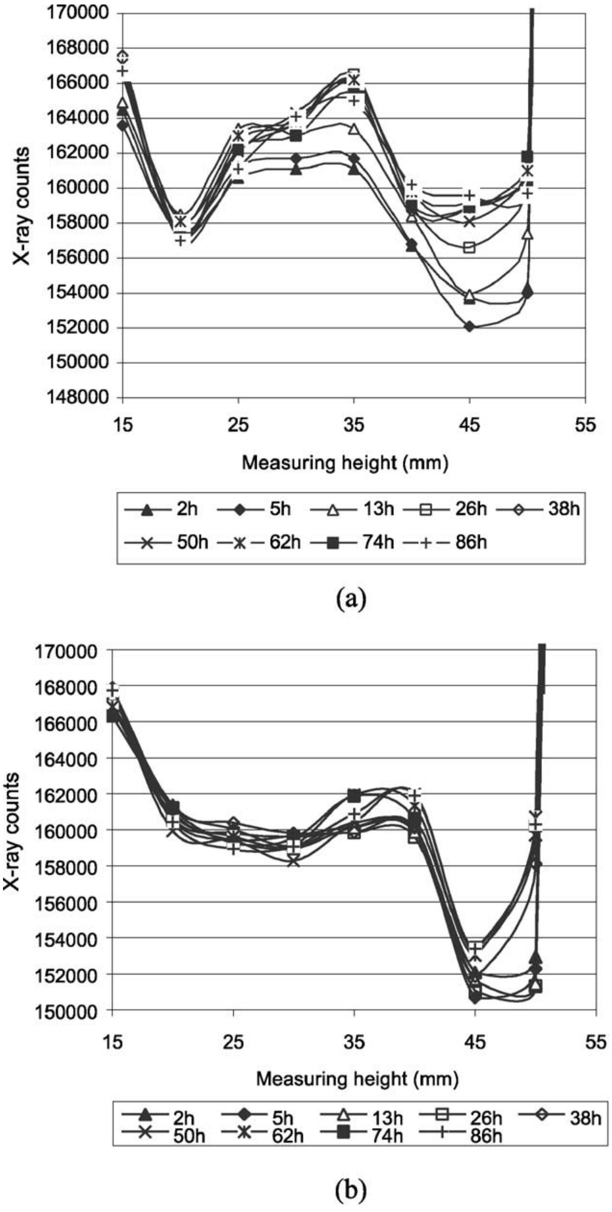


Fig. 2. Density gradient for w/c 0.32 pastes as function of maturity. (a) "paste32a"—open sample; (b) "paste32b"—capped for 26 h before exposure.

The curves are distinct from each other for all "a" samples at early ages (before 26 h or so), as indicated in Fig. 2(a). However, a close proximity of curves is observed for older-age specimens. Hence, the evaporation rate of the water is very high in the first day after casting and is drastically reduced afterwards due to formation of a microstructure that greatly improves resistance of the specimen to moisture loss.

Particular attention shall be given to the top surface of the specimens. A dramatic increase of X-ray counts is reflected by Fig. 2 for all curves at the 50- to 55-mm sections, witnessing an extremely serious water evaporation at the exposed surface of the specimens. The X-ray counts at this location are too high (above 400,000) to be indicated in the picture. This demonstrates the drying penetration to be less then 5 mm. Similar experiments of Bentz and Hansen [3] revealed a drying penetration of about 1.0 mm for an ordinary Portland cement paste sample of 8.4 mm high (4.7 mm wide and 12.5 mm long) with w/c 0.45. The value for w/c 0.30 paste is even lower. In the experiments of Carino and Meeks [5], cylindrical specimens (mortar) with a length of 125 mm and a diameter of 50 mm were split after tensile testing to visually observe the depth of the drying front. His results show that the drying front never penetrated to a distance of 25 mm during the testing period of 28 days. Therefore, it can be concluded that obvious top-down drying only occurs within a small zone near the surface for early age cement paste and mortar.

It should be noted that the experiments performed by Hansen and Bentz [3,4] revealed a leftward shift of the steep gradient (as indicated in Fig. 2) to a location below the surface of the specimens between 0.67 and 4.67 h after mixing. This is corresponding to the initial setting stage. The value of shift for w/c 0.30 paste is about 0.2 mm, and 0.4 mm for w/c 0.45 paste. This shift is not observed in our study. One reason is that the measurements started at 2 h after mixing. And another reason is that the interval of X-ray scanning is 5 mm in this study while Bentz and Hansen chose an increment of 0.2 mm along the vertical axis of the specimen. Therefore, it is suggested to start the recording of X-ray counts as soon as possible after mixing (e.g. within 0.5 h) and to use a small increment of vertical scanning to obtain more accurate results.

3.2. Density profile of cement pastes and mortars

The X-ray counts are reduced by those of the first measurement series (at 2 h) to yield the differential density profile (represented as "differential counts"), so as to highlight the changes due to drying. For certain cases, the differential counts have been further processed by normalizing with the first readings of X-ray counts. The "relative change of counts" is obtained, which is expressed in percentage.

Comparison between the global density evolution of paste and mortar specimens with two w/c ratios (w/c = 0.32 and 0.50, respectively) and cured under different conditions (groups "a" and "b") allows examining the influence of the w/c ratio, curing condition and aggregates on the drying process during cement hydration.

3.2.1. Influence of w/c ratio

The relative changes of X-ray counts for pastes in the "a" and "b" groups with different w/c ratios are indicated in Fig. 3. Both "paste32a" and "paste50a" present a steep increase before reaching a plateau of 1.6–1.9%. The density change of "b" samples is limited to a much more moderate range within ±0.5%. This proves that a sealed curing within the first 26 h after mixing greatly reduces the water loss for the "b" group specimens. The effect of the curing conditions will be discussed more extensively in Section 3.2.3. It can be seen from Fig. 3 that "paste32a" reaches its equilibrium state within a shorter period than "paste50a." This is in agreement with the findings of Bentz and Hansen [3,4]. This must be due to the larger amount of evaporable water in paste with higher w/c ratio. Taylor [6] determined the nonevaporable and total water contents of pastes of various cements having different w/c ratios and cured for different lengths of time. According to their theory, the evaporable water in w/c 0.50 paste under sealed curing is 0.273 kg per kg of cement and the value is 0.154 kg per kg of cement in w/c 0.32 paste. Under the same drying conditions, w/c 0.5 paste contains more evaporable water than w/c 0.32 paste. In this sense, higher w/c paste should have higher percentage of water loss. Similar experiments recently performed by Ye [7] with the same technique reveal good results (Fig. 4). The w/c 0.50 paste "0.5 open" (corresponding to "paste50a" in this study) shows a water loss above 1.6% at 54 h, while the "0.32 open" specimen (corresponding to "paste32a" in this study) reached a stable value about 0.6% within 10 h. This is consistent with the conclusions of Bentz and Hansen [3,4] about mass loss measurement by X-ray absorption for cement pastes of w/c 0.3 and 0.45, respectively.

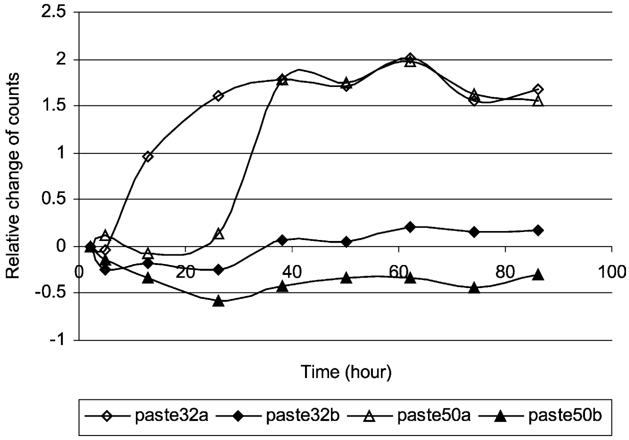


Fig. 3. Relative change of density for pastes of w/c ratios 0.32 and 0.50.

As mentioned above, a threshold of w/c between 0.38 and 0.40 was proposed as necessary condition for complete hydration of cement paste. A mature paste of w/c = 0.38 consists entirely of hydration products. According to Ref. [6], the pastes with w/c < 0.38 consist of unreacted cement and hydration products, while the pastes with w/c>0.38 consist of hydration products and capillary pores. In sealed condition, the global density of cement paste depends to a large extent on the w/c ratio and on the degree of hydration, determining the density of the hydration products.

For a specific weight of unhydrated cement of 3.1×10^3 kg/m^3, a w/c ratio of 0.4, a gel density of $(1.97–2.07) \times 10^3$ kg/m^3 can be calculated. The gel density is found to increase with decreasing w/c ratio. Previous researchers [1] estimated the gel density to be about 2.65×10^3 kg/m^3 for w/c 0.3 paste, and 2.25×10^3 kg/m^3 for w/c 0.5 paste. As hydration progresses, the gel density was found to increase [1]. Theoretically, the density of fresh paste with w/c = 0.32 is about 2.08×10^3 kg/m^3 and the density is about 1.82×10^3 kg/m^3 for w/c 0.50 paste (1.97×10^3 and 1.77×10^3 kg/m^3, respectively, in this experiment). A mature lower w/c paste ends up with a higher gel density. The relative density changes for mature pastes with w/c 0.32 and 0.50 under sealed condition are quite close. This can be proved by the density profiles of "b" group specimens. Hence, the density change caused by water evaporation is more pronounced than the one related to change in gel density.

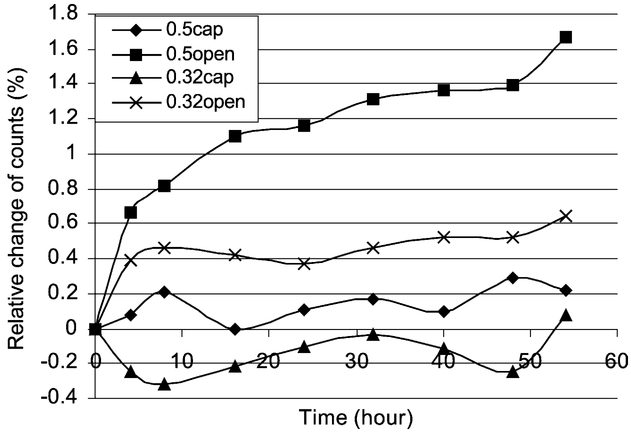


Fig. 4. Relative change of density for pastes of w/c ratios 0.32 and 0.50 (results from a similar experiment in 2002, Ref. [7]).

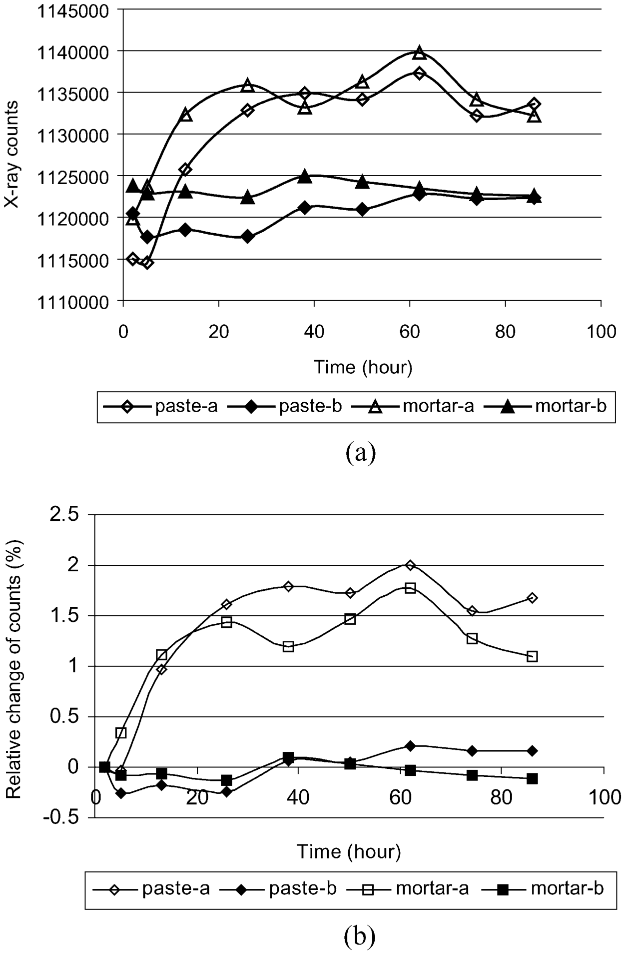
3.2.2. *Influence of aggregates*

The density profiles of pastes and mortars with w/c = 0.32 are shown in Fig. 5, together with the relative changes in the density of the specimens. Mortar specimens reveal slightly higher X-ray counts (Fig. 5(a)) than the corresponding paste samples. This is expected because mortars have less dense structure than pastes due to the incorporation of aggregates. In Fig. 5(b), the higher plateau value of relative changes for the paste (about 1.8% for "paste32a" and 1.4% for "mortar32a") is the result of a slower internal water transport in pastes. The aggregate in mortars increases the transport route because of a larger tortuosity [8]. According to previous research [9], hydration of cement in mortar and concrete proceeds faster than in neat pastes. Faster hydration of cement in the presence of aggregates can be attributed to easier water supply via the porous matrix–aggregate interfacial zone despite the tortuosity-induced increase in transport route. Therefore, mortars are more resistant to surface drying due to good water transport within the specimen. However, the effect of sealed curing is much more important than the tortuosity effect of the aggregate. This is proved by the very small fluctuations for mortars in the "b" group.

It should be noted that the fluctuations of X-ray counts after reaching the plateau value are more pronounced for mortar specimens than for the corresponding pastes. This can be attributed to the relatively small size of the specimens. Evidence from water vapour sorption isotherms [6] indicates that the hydration products are composed of solid units having a size of about 14 nm, with gel pores some 2 nm across. Therefore, the specimen size used in this study (5 × 5 × 40 mm) is acceptable for pastes in reducing structural scatter. However, in the case of mortars, the ratio between maximum grain size of the sand (4 mm) and of the minimum specimen dimensions (5 × 5 mm), violates the rule of having minimum measuring length (of strain gauges) at least four times exceeding minimum specimen dimensions. Hence, the mortar manifests itself as extremely heterogeneous. For more structure-sensitive properties like those involved in the present tests, this ratio should even be (considerably) larger [8]. Therefore, in the presence of aggregates, improvements need to be made in the experimental set-up to guarantee applicability to larger mortar and concrete specimens.

3.2.3. *Influence of curing conditions*

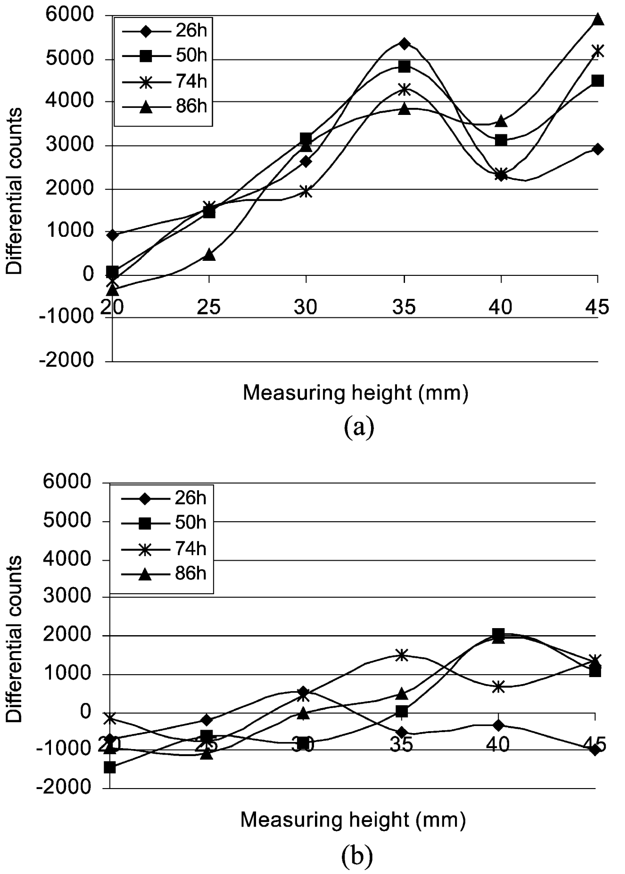
The moisture gradients (represented by "differential counts") within the internal part of the specimens are highlighted in Fig. 6. The readings that are poorly representative of the global density of specimens, such as those at the measuring height of 15 mm (due to wall-effect) and near the top surface at 50–55 mm (due to serious drying), are not shown here. The presence of a drying gradient for "paste32a" is reflected by a positive slope in the differential counts vs. measuring height curves. The curves for "paste32b" do not show a significant slope. A comparison between "a" and "b" samples learns that sealing for 26 h before exposure to the environment has made the material almost impermeable for internal water transport, so that evaporation is greatly reduced. This confirms other experi-



(a)

(b)

Fig. 5. Density evolution for w/c 0.32 pastes and mortars. (a) Data of X-ray counts; (b) Relative change of X-ray counts.



(a)

(b)

Fig. 6. Differential density profiles (relative to 2 h) for w/c 0.32 pastes. (a) “paste32a”—open sample; (b) “paste32b”—capped for 26 h before exposure.

mental observations that one day of sealed curing has a major effect on diminishing the risk due to evaporation (e.g. cracking). Carino and Meeks [5] stated that only one day of moist curing is sufficient to ensure adequate strength development at 25 mm from the exposed surface for w/c ratios between 0.30 and 0.45. Bentz and Hansen [3] also found that shorter curing periods may be sufficient to minimize the water loss for concretes with lower w/c ratios. This is in agreement with the conclusions of Meeks and Carino [10].

Sealed or wet curing at early age of hydration is more important in the application of high-performance concrete. Powers [11] suggested that concrete only needs curing until the capillary pore system de-percolates. The lower the w/c ratio, the sooner this de-percolation will occur in the hydration process. In the case of high-performance concrete with low w/c ratios, it is very important to minimize the evaporation of water from the cement surface during the first day of hydration. If a paste having w/c < 0.44 is cured under sealed conditions, there will be insufficient water to fill the gel pores completely, and the capillary pores will be empty. The effective RH will be low, and hydration will become very slow or will stop, even though free space remains. Even at higher w/c ratio under sealed conditions, partial emptying of the capillary pores will retard hydration, and can produce irreversible changes in pore structure, which reduce the final strength. Furthermore, as cement paste hydrates under sealed conditions, it undergoes self-desiccation due to chemical shrinkage (the reaction products occupying less volume than the reactants) [12,13]. Thus, in high-performance, low w/c concretes, there may be insufficient internal water for complete curing, so that additional water supplied from the exterior surface could greatly enhance final properties. In case of high-performance concrete application, wet curing or sealed curing in the first day is therefore strongly recommended. In view of durability risks, this is especially important since it is the top layer of the concrete that will provide the first protection against the hostile environment.

4. Conclusions

1. The moisture gradient in the cement specimens subjected to surface drying reveals complicated characteristics because mechanisms involving in this drying process influence each other, and hydration changes the material body in a nonlinear way. In general, the moisture gradient changes as function of location and of time, as demonstrated by the present experiments.
2. Pastes and mortars, which are exposed to the environment at the free surface immediately after mixing and casting (“a” group), reveal rapid water loss and density decline during the first 26 h. Thereupon, the drying rate is relatively stable at a low level. Pastes and mortars with a higher w/c ratio (w/c = 0.50) show higher weight losses.
3. Pastes and mortars in the “b” group present very moderate density changes and strongly reduced water losses. Hence, the curing conditions have a significant influence on performance of cements and concretes. Therefore, sealed curing in the first day is strongly recommended, particularly for low w/c ratio cements and concretes.
4. X-ray absorptiometry is useful for the determination of the moisture distribution and the drying profile of cement-based materials. However, the experimental set-up needs to be slightly modified for mortar and concrete specimens with larger structural dimensions.

Acknowledgements

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