'Active' Thin Sections

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Optical microscopy using thin sections has become more and more important over the last decade to study concrete. Unfortunately, this technique is not capable of studying actually hydrating cement paste. At Delft University of Technology a new technique has been developed using 'active' thin sections. This technique allows microscopic observations of physicochemical processes during the first hours of hydration. This paper describes the construction of active thin sections and its development during a research project on the occurrence of syneresis, a known phenomenon from the field of colloid chemistry, in cement paste.

Keywords: **active thin sections, syneresis, early hydration, chemical admixture, mineral addition.**

1 Introduction

Over the last decade, thin section microscopy has become more and more important to analyze concrete samples, especially in the field of damage assessment [1]. Thin sections are made from the end product: hardened concrete. This technique does not allow to study the processes occurring in the paste, which is essential for the formation of the microstructure of the hardened cement paste.
A thin section technique which enables microscopic observations of processes of the first hours after mixing would be valuable, especially since researchers have become increasingly aware, that the physicochemical processes during the first hours of hydration play a very important role in the final structure of hardened cement paste. At Delft University of Technology such a method has been developed. Using 'active' thin sections early processes in cement paste can be studied while the cement paste is hydrating. The method turned out to provide valuable information on the behaviour of hydrating cement paste.
The technique was developed during the research on the occurrence of syneresis, a known phenomenon from the field of colloid chemistry, in cement paste. First descriptions of the development of this technique can be found in references [2, 3]. The current paper describes the construction of active thin sections and its development in experiments to show the presence of syneresis in cement paste. Its strongest point, the observation of early physicochemical processes in cement paste, is demonstrated by showing the influence of mineral additions and chemical admixtures on the hydrating cement paste. Since the active thin sections have been used in the research to gather evidence on the occurrence of syneresis in cement paste, first a brief introduction on the syneresis process is given.

HERON, Vol. 44, No. 2 (1999) ISSN 0046-7316

2 Syneresis

In colloid science, syneresis is a known phenomenon of freshly prepared gels. Syneresis is defined as the contraction of a fresh gel network under the expulsion of its liquid, while the total volume of the system remains constant. The effect was first observed in gels of silicic acid by Thomas Graham [4].

To form an idea about syneresis in cement paste, two stages should be kept in mind. First, upon casting rapid flocculation occurs (within minutes) and a complete network of cement particles is formed in which most particles tend to be linked to only two or three others (see figure 1a). The network contains a substantial amount of entrapped water. During the second stage, due to the same forces that lead to flocculation, but now on a longer time scale (hours), the network tries to rearrange itself. Since the particles are still entrapped in a loose network, the residual attraction forces try to form a denser packing. This much slower, second flocculation process, in which the cement particles move closer together and increase the number of contacts per particle, is known as syneresis. The imbibed water first caught in the network is forced out as syneresis liquid (see figure 1b). Syneresis stops due to the ongoing hydration process (days). The network can only contract when it is still flexible. Once the cement paste has set, the network can only harden and become more rigid.

The idea of syneresis being active in cement paste is not new. In 1935, it is Lea [5] who remembers Michaelis' suggestion on a set cement as being a colloidal gelatinous mass that hardens as it dries and shrinks. Next, in discussing the setting, hardening and ageing processes, Lea states: "It is possible that the gel initially formed undergoes a spontaneous shrinkage, accompanied by syneresis as occurs with silica gel, but there is no definite evidence to show this. In any event, any such change is likely to be over within a few hours of the formation of the gel mass."

A more thorough description of the theory on syneresis in cement paste will be presented in a later paper.

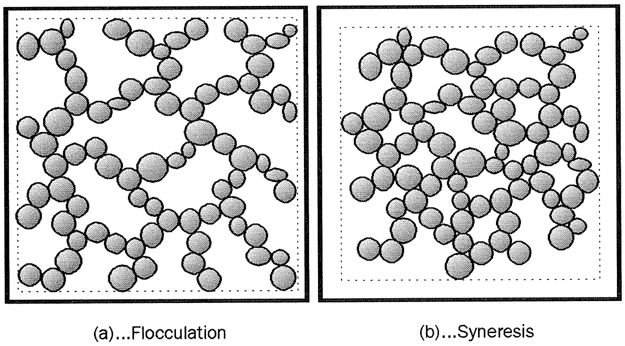


Fig. 1. *Model of the flocculation and syneresis process in cement paste. The total volume remains constant, while the movement of particles closer to each other during syneresis results in the expulsion of water from the network of cement grains.*

3 Development of an active thin section

In the period that syneresis might be present in cement paste, at least two other processes are known to exist: bleeding and chemical shrinkage. Bleeding is a segregation process driven by gravity: the heavier particles sink through the water to the bottom; the water stays behind. Chemical shrinkage

(*i.e.* hydration shrinkage) is due to the fact that the hydration products have a smaller volume than the combined volume of their original components, cement and water. In determining the occurrence of syneresis in cement paste, syneresis should be distinguished from the former two processes.
Syneresis works in three directions, while bleeding only occurs in one, the gravitational direction. If a droplet of cement paste is used, of which the diameter is much larger than its thickness, the syneresis forces should prevail over the gravitational forces, at least in the horizontal plane. Therefore, it was decided to study the syneresis phenomenon in the horizontal plane. To distinguish between chemical shrinkage and syneresis the total volume can be used: syneresis does not change the total volume, chemical shrinkage does. During the syneresis process, as the network contracts, the solid particles move through the liquid. This relative movement of the solid and the liquid is difficult, because friction is generated in the small pores of the network. As a result, a pressure gradient develops [6]. When a droplet of cement paste is considered, the smallest pressure gradient is at its rim. Here, syneresis will show up most clearly, leaving a rim of water at the outer side. This process should be visible under a microscope.

When a droplet of cement paste is studied under a microscope, the droplet is very sensitive to evaporation of (syneresis) water and carbonation. Therefore, the droplet should be protected against the environment, which means the examination should be done in a closed system. By including the decision to study the process in a horizontal plane, a basic concept for a very small flat box is obtained. The size of the box should not be hindering the freedom of motion of the cement particles. The space between the bottom en the lid should be ample enough to allow free motion. This is obtained by the introduction of a 'spacer'. For the thickness of the spacer, a compromise has to be made between the free mobility of the particles and the suppression of bleeding. Here, a thickness of 100 μm has been chosen.

The complete build up of the very small flat box is shown in figure 2. This set up is called an 'active thin section'. By placing a fresh cement paste droplet in the hole in the centre of the spacer (see figure 2) just before the cover glass is placed, the syneresis process in the hydrating cement paste should be visible under a microscope.

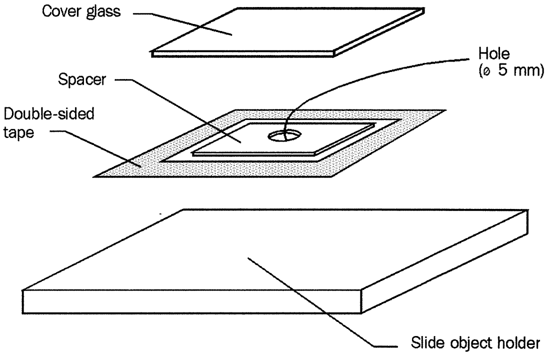


Fig. 2. Schematic build up of an active thin section. The cement paste droplet is placed in the hole in the centre.

Berger *et al.* [7, 8] had done experiments with a similar set up in the early seventies to study the development of portlandite crystals and their influence on crack patterns through C-S-H. In their set up, they placed cement paste in between two glass plates. After pressing the two plates together, they glued the sides of the glass plates to protect the system against fast water evaporation and carbonation. However, the way Berger *et al.* built their package immobilized most of the cement particles. For the detection of syneresis this is not allowed.

4 Experimental procedure

Before an active thin section is placed under a microscope, a sequence of actions has been performed. It starts with a cleaned perspex object slide holder. It is cleaned with water and detergent and dried using compressed air. Then, the double-sided tape is cut in form and placed on the object slide holder; the same is done for the spacer.

Following, the cement paste mixture is prepared. Using a 'watch glass' and an analytical balance (Mettler, type B5, accuracy 0.0001 g) an amount of 1 g of cement and the necessary amount of (demineralized) water is weighed and mixed. The mixing is done by hand using a spatula. This spatula is also used to place one droplet of the cement paste mixture inside the hole of the spacer. After that, the cover glass is placed and pressed flat against the spacer. Since the mixing keeps destroying the flocculating network, the moment of closing the lid is taken as the start of the syneresis process (much like the actual casting of concrete is taken as the start of the microstructure formation of concrete). Now the active thin section is ready to be placed under the microscope.

An optical microscope (Leitz, DM RXP from Leica) connected to an image analyser (Quantimet 500+ Colour Image Analyser from Leica) is used to collect images over time of the rim of the cement paste droplet. An example of what is shown on such an image is given in figure 3. The images are

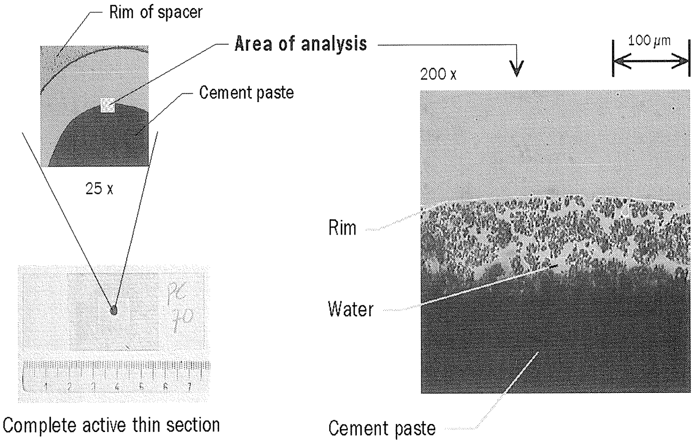


Fig. 3. Example of the area of analysis obtained from the active thin section.

taken at a typical magnification of 200x. During preliminary experiments, it was noticed that the heat of the microscope light influenced the process inside the active thin section. If the light was left on, the small volume heated up and the rate of the process increased. Therefore, during subsequent experiments, the light was only put on to take a picture. The first image was usually taken between five and ten minutes after first contact between water and cement.
The sequence of images are used to calculate an amount of syneresis (see section 6).
To calculate the amount of syneresis the total area of the complete droplet has to be known. This is measured when the experiment is finished by using a macro lens to take a picture of the complete droplet. The error introduced by the resolution of the camera is in this case larger than the error introduced by measuring the contracted droplet instead of the original droplet. The area of the droplet is calculated by the image analyser software.
All experiments are performed in duplicate. If they don't match at least a third experiment is done.

5 Indication of syneresis in cement paste

To investigate the occurrence of syneresis in cement paste, the experimental setup was configured to show the appearance of a water-rich rim at the edge of a cement paste droplet. In the results of preliminary experiments (see figure 4), there appeared to be indeed expulsion of water and contraction of cement particles. However, it can be noticed from figure 4 that the expulsion of water goes over the original rim, which was not expected.

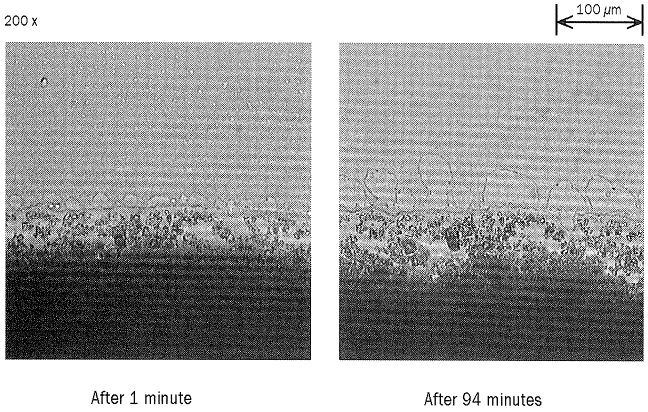
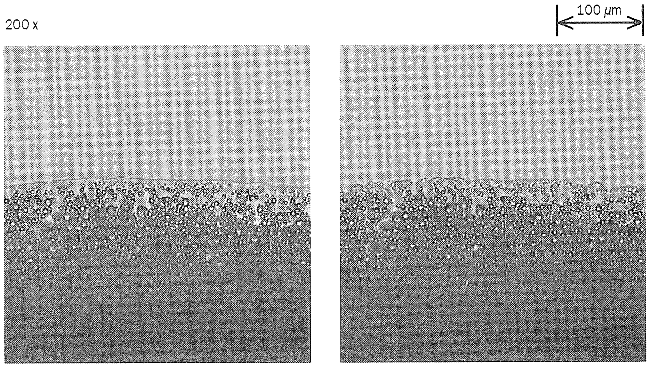


Fig. 4. Expulsion of water from a cement paste droplet (w/c = 50). A glass slide object holder was used as the substrate holder. Time is time after closing the lid of the active thin section.

In other experiments pastes were investigated of only fly-ash and water in the similar ratio normally used for cement and water. Fly-ash was chosen, because it has a particle size distribution comparable to cement, but does not react with water by itself. The result is shown in figure 5: the water and cement particles remain within the initial rim; there is no 'leakage'. The slightly more wrinkled rim at the end of the experiment is due to the slow water loss out of the concealed section. Over the period of eight hours, the water loss is considered to be almost none. The experiments with fly-ash showed that nothing observable appeared to be happening in this system. The absence of 'leakage' could very well be due to the fact that the fly-ash system has much higher cohesive forces than the cement based system. In that way, the capillary suction within the fly-ash paste prevails over the wetting ability of water on glass.

During discussions over this problem, it was realized that the water outside the original rim of the paste droplet was the result of the competition of the surface tension of the glass and water and the cohesion forces between the solid particles and water. It was suggested that the 'leakage' of water beyond the initial rim could be influenced by changing the contact angle with the substrate material. Therefore, the glass slide object holder was replaced by a perspex slide object holder. This time, when the experiments were performed, the original rim stayed in place and there was no more 'leakage'. Furthermore, the cement contraction seemed to occur more easily, probably because there was less adhesion with the substrate.

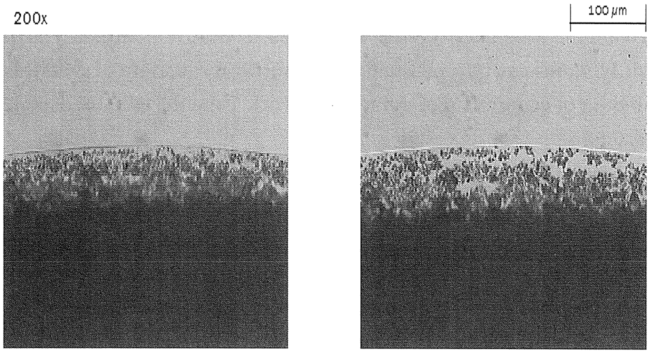
In figure 6, an example is shown of the observed process using a perspex slide object holder. The sequence starts with the first available image, once the active thin section is placed under the microscope (figure 6a). In figure 6b and 6c the cement paste contracts, while water accumulates at the rim. In figure 6d the water area breaks up, most probably due to the started chemical shrinkage, which induces that the water is sucked into the hydrating cement paste.



After 1 minute After 476 minutes

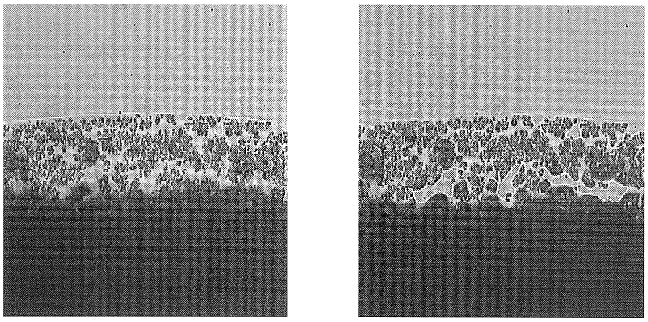
Fig. 5. Lack of water expulsion from a mixture of fly-ash and water (fa/w = 0.50). A glass slide object holder was used as a substrate holder.

This process continues in figure 6e, until in figure 6f, all the free (visible) water has been sucked in. On the process shown in figure 6, the following can be noted. The process occurred in a horizontal plane, so there was no interference due to bleeding. The process took place in the first few hours after mixing, while the network was still flexible, before the cement paste had set. The experiments did show a contraction of the solid cement particles, while water accumulated near the rim. The spacer material made sure there was a constant thickness between the slide object holder and the cover glass; ergo, the cement paste droplet had a constant thickness. The original rim stayed in place and since there was a constant thickness, this meant that the volume did not change (no chemical shrinkage at first). All together, the process shows great similarity with a well known phenomenon in colloid science called syneresis.



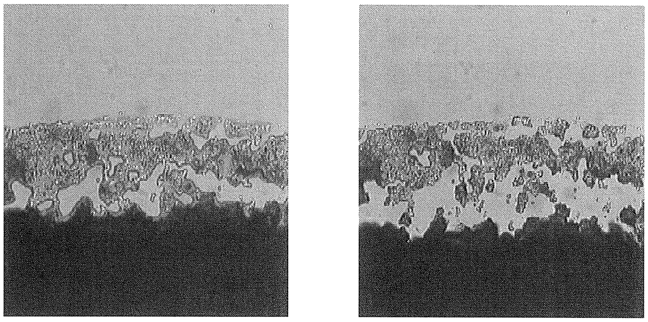
a) After 1 minute

b) After 13 minutes



c) After 44 minutes

d) After 54 minutes



e) After 65 minutes

f) After 93 minutes

Fig. 6. *Process of the contraction of cement particles, while water first accumulates at the rim and later is being sucked into the hydrating cement paste. A perspex slide object holder was used a substrate holder.*

6 Calculating the amount of syneresis

To be able to compare different experiments with each other, it is necessary to quantify syneresis. The amount of syneresis can be quantified by measuring the amount of syneresis liquid, or by determining the amount of contraction of the solid network. Here the amount of contraction of the cement paste is used.
Syneresis can work in all three directions. However, by the set up of the active thin section, the thickness of the cement paste droplet is assumed to be constant through the usage of the spacer. Since the thickness of the cement paste droplet remains constant, the measurement can be reduced from a volume problem to an area problem. Next, if a polar coordinate system is used instead of a Cartesian coordinate system, the contraction of the cement paste droplet can be expressed in one dimension, the radius reduction (Δr). Using this radius reduction and the initial radius of the complete cement paste droplet (*R*), the amount of syneresis in volume percentage follows from equation (1):

$$\begin{aligned}\text{Syneresis (vol\%)} &= \frac{\pi R^2 - \pi(R-\Delta r)^2}{\pi R^2} \times 100\% \\ &= \frac{2R\Delta r - \Delta r^2}{R^2} \times 100\%\end{aligned} \tag{1}$$

The initial radius of the complete cement paste droplet is calculated from the measured area of the complete cement paste droplet. To calculate the radius reduction, different microscopic images are used that have been collected at the same location of the rim of a cement paste droplet during an experiment. In figure 7 the necessary parameters for the calculation are identified.

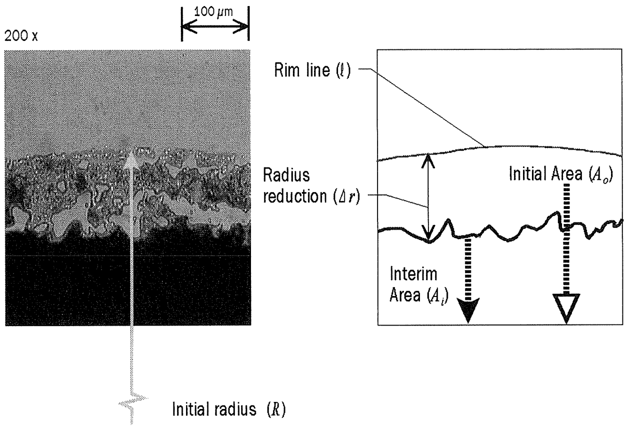


Fig. 7. Nomenclature for the calculation of the amount of syneresis.

Using a calibrated image analyser, the amount of cement paste within the image is determined based on a threshold value of the light intensity. In the series of images from one experiment the amount of cement paste present in the image area decreases, see figure 6. Using the first image of an experiment series, the initial cement paste area (A_o) is determined. In subsequent images during the same experiment, as the cement paste contracts, intermediate areas (A_i) are measured. Subtraction of an intermediate cement paste area from the initial cement paste area gives a contracted area ($A_o - A_i$). This contracted area can be approximated by a rectangular, given the initial radius (R) of the complete cement paste droplet to be usually around 1500 μm. The contracted area can be divided by the width of the image (350 μm) to calculate the radius reduction. This will give a small overestimation of the radius reduction. Another way of calculating the radius reduction is by dividing the contracted area by the rim line (l). In this case the radius reduction will be slightly underestimated. To compromise between the differences, the choice has been made to use the mean value of the width of the image and the rim line in order to calculate the radius reduction.
An error analysis on this calculation has been made. The parameter study showed that the amount of syneresis is determined with a relative error of 17%. A statistical review of an experiment that was repeated eight times showed that the actual error is about 11% for the total amount of syneresis. This error is considered to be small enough for the moment to compare the different experiments and to watch for trends. However, to rely on the currently calculated amount of syneresis as a solid textbook value would over validate the current set up. The accuracy of the calculated amount of syneresis is currently governed by the error in the camera of the image analyser. To reduce the error a camera with a higher amount of pixels detection per square millimetre is necessary.
To compare the results of the various experiments, the calculated amount of syneresis is plotted versus the time into the experiment. In those graphs it is found sometimes that the amount of syneresis decreases towards the end of the time scale. This decrease is due to an artificial error introduced in the calculation procedure. The amount of syneresis is calculated based on the reduction of the area occupied by the cement paste at different times. The reduction in area is determined by the image analyser using a threshold value on the light intensity of the obtained image. However, some cement particles remain behind in the outer rim of the cement droplet. When these particles start to hydrate and form C-S-H, they are blocking more light over a larger area. The image analyser then calculates more paste to be present within the image than before, which results in a smaller calculated amount of contraction, ergo, a smaller amount of syneresis.

7 Influence of additions and admixtures

Various mixtures have been tested during the research program on the occurrence of syneresis in cement paste. Part of the experimental program consisted of series in which mineral additions, chemical admixtures or both were added. In this section a small review is given on those experiments to illustrate the capability of the active thin section in studying the general effects of the different additions and admixtures in the early hours of hydration.
First mineral additions are discussed. Ground granulated blast furnace slag, quartz flour, silica fume and fly-ash have been tested. The standard cement mixture consisted of CEM I 32.5 R cement and a water/cement ratio of 0.50. The ground granulated blast furnace slag cement used was CEM

III/B 42.5 LH HS which contains a slag percentage of about 70%. A non-porous alpha quartz flour has been used to study the effect of an inert mineral addition. The silica fume was provided in a powdered form of grey pellets. The fly-ash was a German EFA-Füller fly-ash from a wet-bottom powder coal plant. The water/solid ratio for all mixtures was always 0.50, which was obtained by replacing part of the cement by the mineral addition under investigation. Typical results are presented in figure 8.

From the results it can be learned that most mineral additions show no influence on the contraction of the cement paste. Only the use of quartz flour gives a remarkable increase in the amount of contraction. From experiments with 100% quartz flour replacement it was found that this quartz flour has a strong tendency to contract by itself. The use of ground granulated blast furnace slag cement showed a slight increase in the amount of contraction. It might be interesting to investigate whether or not this could be the origin of the denser microstructure resulting in substantially lower permeability compared to the use of plain Portland cement.

For chemical admixtures only two different admixtures have been used: a commercial naphtalene sulphonate based superplasticizer (OFT3 from Tillman BV Chemische Bouwstoffen) and a commercial air entrainer (MicroAir 100 from Master Builders PCI bv). The superplasticizer has been added in 1.5% by mass of cement and the air entrainer has been used in 0.50% by mass of cement. Typical results of the experiments are presented in figure 9.

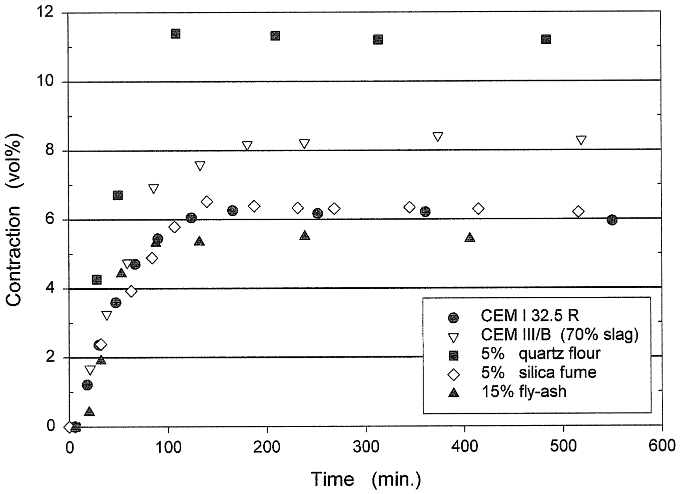


Fig. 8. Typical results for the influence of various mineral additions on the contraction. The water/solid ratio of the mixtures was 0.50 in all cases. Given percentages are percentages of cement replacement.

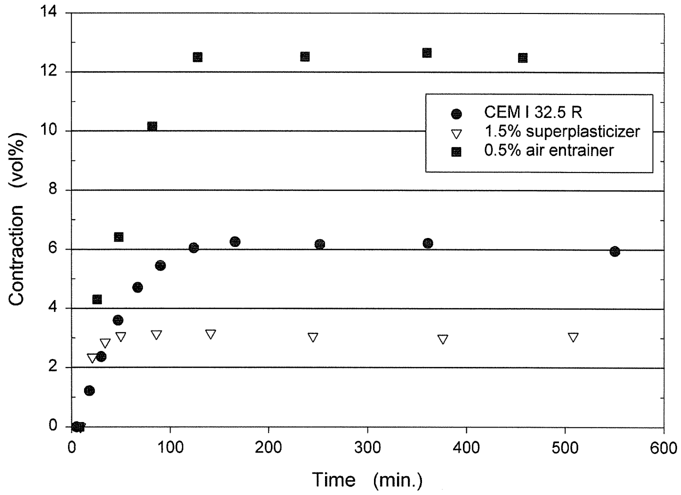


Fig. 9. Typical results for the influence of various chemical admixtures on the contraction. Amounts used are 1.5% superplasticizer by mass of cement and 0.50% air entrainer by mass of cement. Water/ cement ratio was 0.50.

The results show that the chemical admixtures have a large influence on the contraction. The use of superplasticizer decreases the amount of contraction. This can be understood through the syneresis model given in figure 1. Superplasticizers are known to counteract the effect of flocculation. When the flocculation process is disturbed it has a large influence on the subsequent syneresis / contraction process. The effect of air entrainer leads to a much higher contraction. The reason for this is at present not completely clear. It might be that part of the air bubbles collapse and thus give a much higher contraction. However, this is still under investigation.

8 Conclusions

Using the active thin section technology, the very early physicochemical processes in cement hydration can be studied. It is shown that within a droplet of cement paste the solid cement particles do withdraw from the outer rim of the droplet, leaving a water-rich zone. This process appears to be similar to syneresis, a phenomenon known from colloid chemistry. Furthermore, it is shown that additions like ground granulated blast furnace slag, fly-ash and silica fume do not change the contraction process much. However, chemical admixtures, like the superplasticizer studied, seem to have a substantial influence.

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