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# Active thin sections to study syneresis[1]

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**Abstract**

Thin sections are made from hardened products. To achieve information on the very early hydration process of cementitious composites, one would need an "active thin section," i.e., a thin section of a cement paste that is hardening while under investigation. In our research, it has been possible to construct such active thin sections. Using ordinary light microscopy it is possible to observe water movement and volume changes on hydrating specimens of about 100-μm thickness. This research is part of a larger project to investigate the formation of the interfacial transition zone. We believe that a process called syneresis might play an important role. Syneresis is the contraction of a gel under the expulsion of a liquid. This is addressed in the second part of this paper. This phenomenon is studied using active thin sections. 

*Keywords:* Active thin sections; Cement paste; Interfacial zone; Syneresis

In the field of concrete chemistry, a growing number of scientists are focusing their research on the first day of hydration. This originates from the knowledge that concrete properties are basically formed during this early part of the hydration process.

The investigation of the early hydration of cement paste is very complex. The number of variables seems to be endless and keeps changing constantly. For some reason, a researcher is inclined to accept results more eagerly when observed by the eye; if one can see the process, it somehow reduces the complexity of a problem.

The investigation of cement hydration also has encountered this phenomenon, and two main groups come to mind: electron microscopy and optical microscopy. The usefulness of the scanning electron microscope (SEM) has been demonstrated many times [1–3]. However, until about a decade ago, the SEM could only be used on coated, dried specimens. Only with the introduction of the environmental-SEM (E-SEM), which can handle uncoated and even wet specimens, was a new period in cement and concrete research reached [4,5].

Next to electron microscopy, a similar process is found in optical microscopy. In petrographical studies, thin sections of concrete have been used for many years to obtain results on a meso level and sometimes unique information, especially in the field of damage analyses [6]. Unfortunately, for this technique the cement paste needs to be hardened, so no information can be collected on the hydration process.

In this paper a description is given of a new technique using an "active thin section." A thin section prepared in this way allows cement paste to hydrate in normal conditions while under investigation. We used these active thin sections to study a phenomenon known in the field of colloid chemistry as syneresis. This phenomenon is described in the second part of this paper.

This research is part of a larger project to investigate the interfacial transition zone. We believe syneresis might be an important process in the formation mechanism of the interfacial transition zone.

## 1. Thin sections

To prepare samples for thin section analyses, a procedure typically is used in which the samples are impregnated in an epoxy resin under vacuum and are cut and polished to a thickness of about 30 μm. The epoxy resin is necessary to preserve the form stability of the sample (and can be mixed

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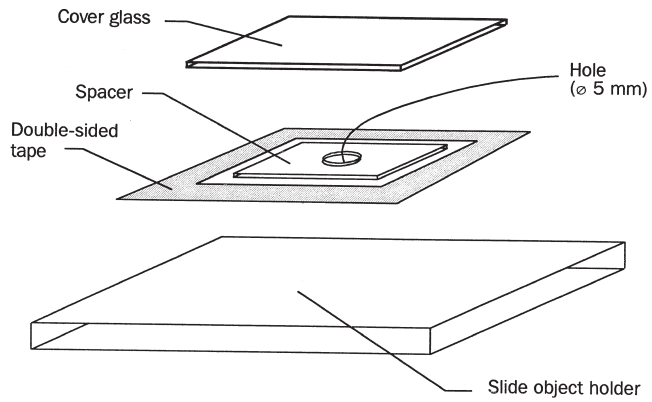


Fig. 1. Schematic buildup of an active thin section.

with fluorescent dye for easy detection of cracks and pores). A known thickness is important for the qualification of minerals under polarised light and usually is determined on the colour shift of quartz.

By using thin section analysis, specific information can be obtained on concrete quality and damage analysis. It is a relatively fast way to determine quality control of aggregates as well as concrete damage due to alkali-silica reactions, sulfate attack, or freeze-thaw. The accuracy of the results depends on the experience of the researcher [7,8].

In the 1970s, Berger and McGregor [9] Berger et al. [10] used a form of thin section technique to study cement paste. In their research, two glass plates were pressed together, thus immobilising the cement particles. Because they were interested in the portlandite crystals and the crack patterns through C-S-H, mobility did not matter as much. However, in our research, the ability to allow movement of the hydrating cement paste is of essential importance. This will become clear in the second part of this paper. Naturally, the hydrating cement paste should be protected against fast water evaporation as well as carbonation. Furthermore, it would serve the investigation well if the possible three-dimensional movement was brought back to the easier to detect two-dimensional movement.

These three demands (free motion, concealed, and forced two-dimensional) led to a schemetic buildup of an "active thin section" as shown in Fig. 1. A drop of normal cement paste composition (w/c ratio = 0.5) is placed inside the hole just before the cover glass is placed. The spacer is used to ensure a thickness of 100 μm exists between the two plates. Because well over 90% of the cement particles are smaller than 100 μm, this leaves enough space for motion while it is also thin enough to provide for a two-dimensional system.

To check if pseudobleeding[2] would occur in the 100-μm thick droplet, an experiment was set up, consisting of just fly ash and water in a similar ratio normally used for cement and water. Fly ash was chosen because it has a similar particle distribution as cement, but it does not show any reaction with water by itself. In Fig. 2, the rim of the droplet is shown at the start and at the end of the experiment. As one can see, the configuration holds; there is no pseudobleeding. The slightly more wrinkled edge at the end of the experiment is due to slow water loss out of the concealed section. Over a period of 8 hours the loss is considered to be within acceptable limits.

## 2. Syneresis

When a system is subjected to rapid coagulation, as normal cement paste is [11], the result is a loose flock in which

[2] With pseudobleeding, here the leakage of water out of the paste system is meant.

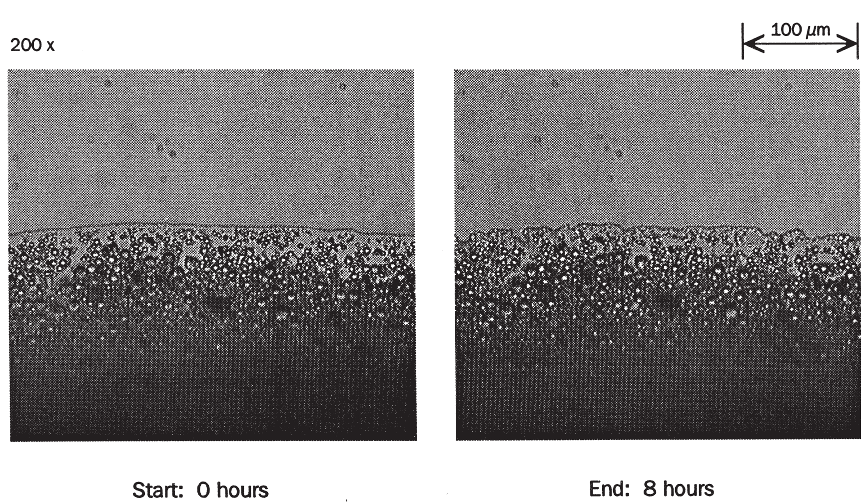


Fig. 2. Check on bleeding with fly ash mixture.

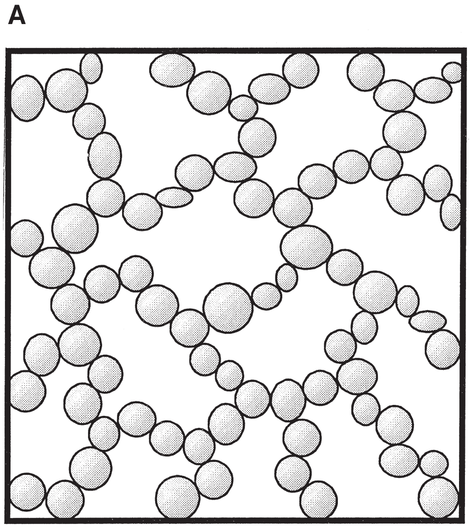


Fig. 3. Representation of the syneresis process. (*A*) Open structure. Particles are only linked to two or three other particles. (*B*) Increased number of contacts in contracted structure.

most particles tend to be linked to two or three other particles. The structure of these flocks is tenuous and contains a substantial amount of entrapped water. The free energy can be decreased by formation of a greater number of contacts. This entails contraction of the dispersed phase. The volume of the dispersed phase is decreased and water is spontaneously expelled from the flocks. This phenomenon was first referred to as syneresis by Thomas Graham [12]. Fig. 3 shows schematically the syneresis process of a cement suspension.

The idea of syneresis being active in cement paste is not new. In 1935, it is Lea who remembered Michaelis' suggestion of a set cement being a colloidal gelatinous mass that hardens as it dries and shrinks. Next, in discussing the setting, hardening, and aging 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" [13].

A common example of syneresis is found in the dairy industry. Gels formed from milk by renneting or acidification under quiescent conditions subsequently may show syneresis, i.e., expel liquid (whey), because the gel (curd) contracts. Under quiescent conditions, a rennet-induced gel may lose two thirds of its volume, and up to 90% or more if external pressure is applied [14]. Often, syneresis is undesired, e.g., during storage of products such as yogurt, sour cream, cream cheese, or quark. On the other hand, in making cheese from renneted or acidified milk, syneresis is an essential step.

Another example of syneresis is the formation of a blood clot. When blood flows out of its vessel and comes into the open, a complex system of reactions turns albumins into a network of fibrin fibres. Into this network, platelets are trapped and they are mainly responsible for the contraction of the network to about half its original volume, meanwhile squeezing out the blood serum.

## 3. Experiments

To investigate the existence of syneresis in cement paste, the active thin sections were used. In Fig. 4, a top view is presented of an active thin section. The cement paste droplet is clearly visible in the centre. Using a Quantimet $500^{+}$ Colour Image Analyser from Leica, the (rim of the) cement paste droplet can be examined during hydration. Because the thickness of the cement drop is negligible compared to its diameter, a two-dimensional system is created. Due to the spacer, the majority of the cement paste can move relatively freely.

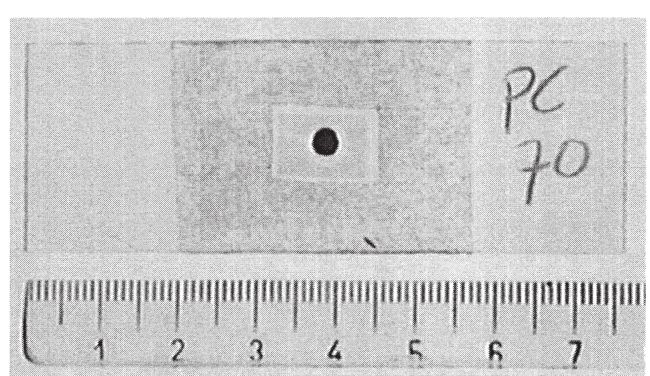


Fig. 4. Top view of an active thin section. The black dot in the center is the cement paste droplet.

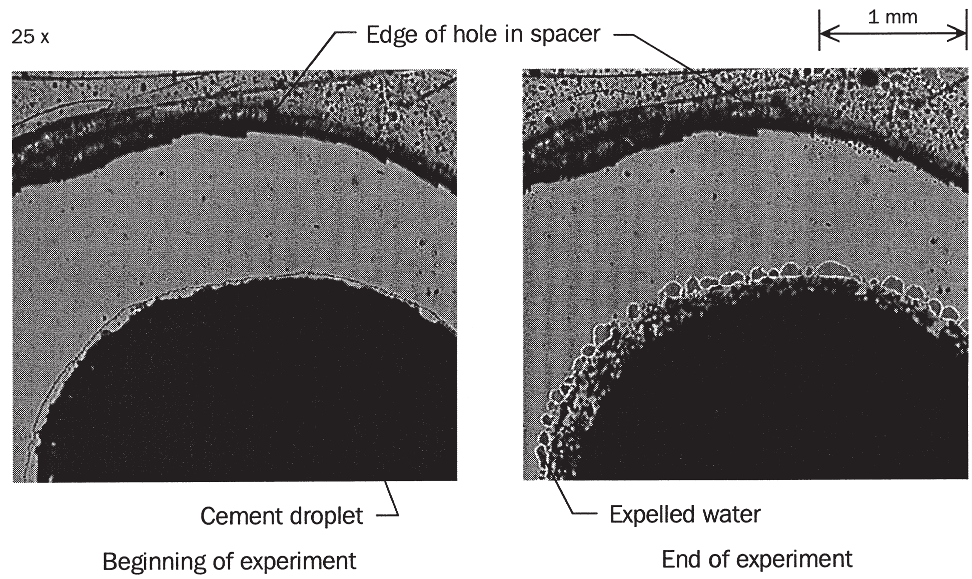


Fig. 5. Cement paste droplet at the start (*left*) and end (*right*) of an experiment.

In Fig. 5, a closer look is taken of the cement paste droplet at a magnification of 25×. The paste is made with CEM I 32,5 R cement and a water/cement ratio of 0.50. The photograph on the left was taken at the beginning of the experiment, whereas the one on the right was taken about 8 hours later. Even at this magnification the large effects can be observed.

The investigation is performed typically at a magnification of 200×. Some first results look like the photographs shown in Fig. 6. Compared to the photographs taken from the fly ash experiment (see Fig. 2), there is clearly an expulsion of water present. Therefore, there has to be an active process forcing the water out of the original droplet. However, there is also an interaction between the glass of the slide object holder and the cement, which interferes with the expected contraction of the cement. To solve this problem, we currently are running experiments in which we changed the material of the slide object holder from glass to PMMA (Perspex).

## 4. Conclusion

In this paper a new technique using active thin sections was introduced. The technique was developed in a study to

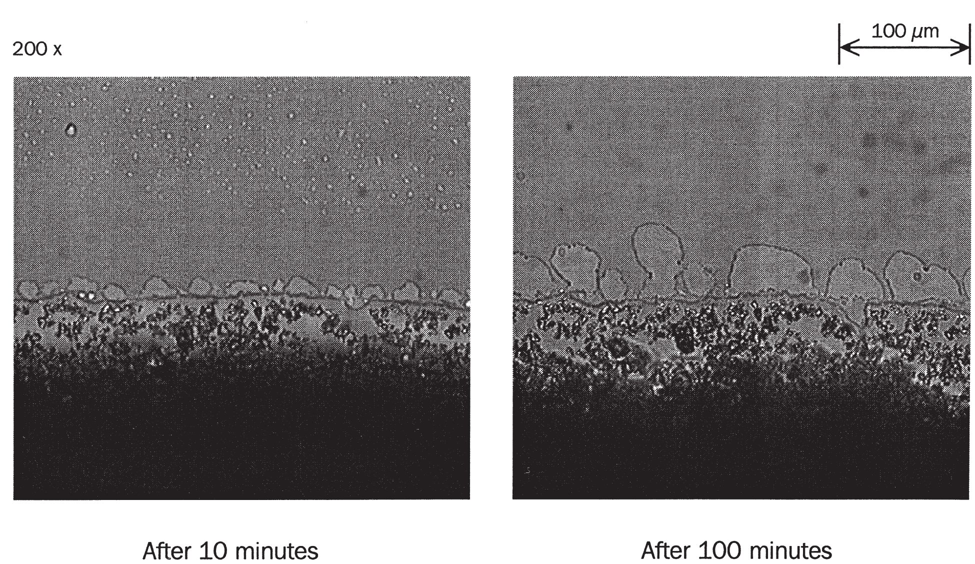


Fig. 6. Water is actively expelled while cement paste is hydrating.

investigate the presence of syneresis in cement paste. The phenomenon of syneresis is (re-)introduced in this article.

Using active thin sections, a first step was made to gather evidence in support of the hypothesis that syneresis might be present in cement paste.

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