SYNERESIS

in

CEMENT PASTE SYSTEMS
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CEMENT PASTE SYSTEMS

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Thesis

Engineers, about fifty years ago, stumbled upon the problem of the bonding between cement paste and aggregates, now known as the interfacial transition zone, which, to date, is regarded as the strength determining weak link in the structure of ordinary concrete.

The interfacial transition zone is part of the hydrated cement paste. Its microstructural characteristics within a plain Portland cement concrete are a high porosity, long ettringite needles and a high amount of relatively large calcium hydroxide crystals. From these characteristics it is considered to be the preferred path for the propagation of cracks in concrete. Furthermore, the high porosity has an important influence on the transport properties of concrete, and as a consequence, on durability.

Maybe the most quoted and least explained theory on the formation of the interfacial transition zone, the wall-effect, cannot explain the width of the interfacial transition zone.

In a perfect stacking of particles a wall introduces mismatches: the so-called wall effect. However, for cement particles with a median particle size of about 15μm, it is impossible to explain an interfacial transition zone with a wide of 50μm on account of the wall-effect. Furthermore, the size of the interfacial transition zone can be changed by adding chemical admixtures. Since the wall-effect is only a matter of packing near a wall, chemical forces are not taken into account. Therefore, the change due to chemical admixtures cannot be explained by the wall-effect. (The details of the discussion are given in appendix I.)

By the absence of a good explanation, syneresis was suggested as an additional hypothesis, which does take into account the chemical effects that are overlooked by the wall-effect.

Syneresis is the contraction of the network in a particulate gel of solid particles, under the expulsion of its liquid while the total volume of the system remains constant. Upon mixing water and cement, dissolution of Ca^{2+} ions lead to conditions for rapid flocculation. Upon casting, a complete network of (hydrating) cement particles is formed in which most particles tend to be linked to only two or three others. In ordinary cement paste, the network contains a substantial amount of entrapped water. Due to the same forces that lead to flocculation in the first place, the network continues to rearrange itself on a longer time scale. This much slower, second flocculation process, in which the cement particles move closer together, is known as syneresis.

It is suggested that, if the expelled syneresis water accumulates near the surface of the aggregates, syneresis might provide the necessary addition to the wall-effect to explain the rather large width of the interfacial transition zone, and introduces the previously absent chemical forces at the same time.
Experiments using specially designed active thin sections indicate that syneresis is present in cement paste.

A very small flat box was specially designed to study hydrating cement paste under a microscope. By studying the process in a horizontal plane, bleeding was excluded. Since syneresis does not change the total volume, but chemical shrinkage does, the difference between these two processes could be detected. Taking images of the rim of a cement paste droplet inside the active thin section and comparing these images over time, indicated that the total volume did not change (at first), while at the same time water and cement paste did separate.

Results of the experiments described in this thesis indicate that the syneresis model seems capable of explaining the effects of mineral additions and chemical admixtures on the physico-chemical behaviour of cement paste.

The structure of the initial network of (hydrating) cement particles formed right at the beginning of the experiments seems to have a major influence on the initial rate and the degree of syneresis. Based on the fineness (i.e. density) of this network and the amount of entrapped water it holds, most of the syneresis results can be explained. By using mineral additions the cement particle network is disturbed and becomes more fragile, leading to a faster initial rate of syneresis. By using dispersion agents like superplasticizers, the flocculation of the initial network is counteracted, thus reducing the degree of syneresis.

Since syneresis is active in the early hours of the hydration process in cement paste, it is most likely that syneresis has a large influence on the eventual microstructure of the hardened cement paste.

Although not investigated in this thesis, the syneresis model developed here could be a useful basis in the fundamental research to understand the microstructure formation of hardened cement paste. The model seems to have the abilities to explain effects of chemical admixtures on the microstructure of hardened cement paste. Hopefully future research will bring more clarity on this part with benefit of the syneresis model.

Mario de Rooij,
March 2000.
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Making concrete in a very basic form requires the mixing of cement, water and aggregates. Concrete hardens because water and cement react. In simplified terms, concrete could be considered as aggregates glued together by hardened cement paste.

At the early 1950's it was discovered that in general the bonding between cement paste and aggregates was very weak. There appeared to be a porous bonding zone, with a width leading up to 50 μm, between the aggregate and the bulk of the hardened cement paste. This zone, now known as the interfacial transition zone, is considered to be a primary defect in concrete and the preferred path for the propagation of cracks. It significantly influences the properties of concrete like tensile strength, modes of failure and bending stiffness. Furthermore, the characteristics of the interfacial transition zone have an important influence on the transport properties of concrete and, as a consequence, on durability.

To improve the properties of concrete, the cause of the problems associated with the weak interfacial transition zone should be known. Based on investigations of the microstructure of the interfacial transition zone (see also chapter 2), the generally accepted idea for the formation of the interfacial transition zone is that at the onset of cement hardening the region close to the aggregate surface has an average less cement grains and is rather filled with water.

To explain the existence of the water-rich layer near the aggregates, a few theories have been suggested (see chapter 2). Currently, the most widely stated theory is the so-called wall-effect. However, calculations show that the wall-effect cannot explain an interfacial transition zone of 50 μm wide (see appendix I). Furthermore, the width of the interfacial transition zone can be changed by chemical admixtures. Since the wall-effect is based only on particle stacking, chemical forces are not taken into account. Therefore, the change due to chemical admixtures cannot be explained by the wall-effect. This limitation was the origin and motive for the current investigation.
1.1. Another approach: Syneresis

About ten years ago, the Materials Science Group of the Civil Engineering Department at Delft University of Technology started to investigate the interfacial transition zone. Larbi [1] made a thorough study of the effects of mineral admixtures on the interfacial transition zone and their effect on concrete properties. At the end of his research project professor Frens, professor of physical chemistry from the Chemistry Department at Delft University of Technology, became involved as a member of the Ph.D. committee. From his point of view he suggested a new idea for the possible formation mechanism of the interfacial transition zone, known in colloid chemistry as syneresis.

Syneresis is the contraction of a fresh gel network under the expulsion of its liquid, while the total volume of the system remains constant. The idea of syneresis being active in cement paste is not new. In 1935, it is Lea [2] who remembers 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.”

In the research carried out for this thesis, the possible existence of syneresis in cement paste has been investigated. If syneresis is present in cement paste, it may add significantly to the understanding of the formation of the typical microstructure of the interfacial transition zone and thus to the reduction of the problems at the weak interfacial transition zone. Since syneresis should be active in the very early hours of hydration, the syneresis process might add to the understanding of the complete microstructure of the hardened cement paste. These aspects are all of prime importance in understanding and improving the properties of concrete.

1.2. Objectives of the research

The objectives of this research are:

1. To investigate the existence of syneresis in cement paste.

2. To develop a model for the physico-chemical behaviour of cement paste during the first hours of hydration, by which syneresis could be explained and understood.
Chapter 2

The Interfacial Transition Zone

At the early 1950's, France was involved in the implementation of a vast rebuilding program, particularly in the development of hydraulic energy. Many large dams, underground works and power stations were built. However, sometimes in galleries dug in very hard granite, which appeared to be stable and dry when they were built, the walls might crumble in some places. At the same time, some of the largest blocks, extracted from the same galleries, stored outside and exposed to the weather, turned into an incoherent clay mass.

Following requests from Electricité de France and other large public work companies, Farran [3] and his group were first prompted to study the main problems of rock weathering, its influencing factors and its measurement and rate, so as to define systematically what type of lining should be used for the underground structures. His studies led to the following results:

1. Microscopic observations of adherence on thin plates cut from mortars made from different pure mineralogical species, clearly demonstrated the influence of the aggregate type on the concrete quality [4].

2. During the setting and hardening of a specific cement in contact with a particular aggregate, some hydrated constituents settled in a specific manner at the area in contact with the aggregate and the contact film type was different from that of the hydrated cement mass [5].

3. According to the cement and aggregate type, specific reactions could occur at their contact point, in mortar or in concrete. Some of these reactions were destructive and others constructive, as a result of the formation of intermediate solid solutions or, even epitaxial attachments [6].

4. For water/cement ratios corresponding to the practical field of composition of mortar and concrete, the aggregates were surrounded by paste of a particular structure, which constituted a transition zone between aggregates and binding material. Besides a composition difference, the texture of the transition zone was looser than the texture of the binding paste and its strength was lower [7]. Farran called this zone (in French) 'aureole de transition'. Some authors still prefer this
name over interfacial zone or transition zone, since 'aureole' covers the meaning of complete encircling, interaction, thickness and gradient of composition, whereas the word 'zone' seems to cover less of these essential ideas. Nonetheless, in this thesis the term interfacial transition zone will be used.

2.1. Microstructural characteristics

* The microstructure

Although the morphology of hydration products in the interfacial transition zone has been extensively studied, there is still no consensus on the interface mineralogy and microstructure. In literature, references are made to interfacial transition zone models from Barnes et al. [8], Ollivier and Grandet [9], Monteiro [10], and Zimbelmann [11]. In this thesis, a composed schematic impression of the interfacial transition zone is made, based upon literature information, which is shown in figure 1. Starting from the aggregate surface going towards the 'bulk' cement paste, the subsequent areas appearing in the interfacial transition zone are discussed here below.

In 1978, using glass as an aggregate, Barnes et al. [8] found a 'duplex film', typically 1 to 1.5 μm thick. On the glass face, calcium hydroxide (CH) crystals developed rapidly with their c-axis preferentially oriented normal to the glass. This layer showed no evidence of individual crystal outlines or boundaries, indicating that the layer is continuous. On the cement paste side, rod-shaped C-S-H gel formed, somewhat resembling hairbrush bristles. The duplex film developed for all Portland cements investigated. However, a generally thinner calcium hydroxide layer was found to form when granulated blast furnace slag cement was used.

Around the same time, Zimbelmann [11] used flat aggregate materials from limestone, quartz, calcite, feldspar and granite. He did not report a duplex film, but introduced a 'contact layer', that is about 2 to 3 μm thick and consists of calcium hydroxide crystals with their (001)-plane perpendicular to the aggregate surface. He further reported the deposition of ettringite needles on the aggregate surface in the initial state of hydration [12]. From his experiments using granulated blast furnace slag cement, he reported the thickness of the contact layer to be essentially smaller than with plain Portland cement.

One of the disputes for consensus is whether or not the duplex film and the contact layer have the same origin, or may be could even be the same, taking the differences back to the different kind of aggregates. Diamond, in a review article [13], has tried to solve the matter by introducing the contact layer as an intermediate between the duplex film and the rest of the interfacial transition zone. However, Zimbelmann's research states that the growth of the calcium hydroxide crystals is terminated after about 16 hours from the beginning of hydration, while Diamond in his review recalls that the new layer develops "after a day or two have elapsed."

Beyond the layer of products attached to the aggregate surface, there is less dispute among scientists. In the very early stages of hydration there is much solution-filled space, only sparsely occupied by cement grains. Even after long periods of hydration the mass content of this water-rich zone remains relatively low (i.e. has a high porosity). Here,
relatively large, hexagonal calcium hydroxide crystals can be found, sometimes tens of microns across but only one or two microns thick, as well as clusters of long ettringite needles [14]. Both Barnes et al. [8] and Zimbelman [11] see the large calcium hydroxide crystals perpendicular to the aggregate surface (i.e. their c-axis is parallel to the aggregate surface). Also, they both report the existence of small stacked calcium hydroxide platelets in much of the remainder of the open space near the duplex film, with their (001)-plane parallel to the aggregate surface. According to Barnes et al. [8] these secondary deposits of calcium hydroxide are very pure and develop after about three days.

Recently, Zampini et al. [15] published results on microstructural changes occurring at the wet paste-aggregate interface up to an age of 24 hours, using an environmental scanning electron microscope. They reported a 'sheaf of wheat' morphology, which is formed as early as five minutes from the time the cement paste and aggregate particles interact. According to their results, this microstructure is an early hydration product formed through precipitation from a supersaturated solution of calcium hydroxide. They suggested that the hydration product is structurally similar to portlandite, but chemically (based on a calcium-to-silica ratio) resembles an early formed C-S-H product. Unfortunately, they do not provide any comparison to observations made by others. The 'sheaf of wheat' morphology seems to resemble C-S-H structures mentioned by Ollivier and Grandet [9], and Monteiro [10]. However, no specific observations are mentioned about large portlandite crystals, ettringite needles or surface layer effects.
Characterisation techniques

Various methods have been developed to investigate the interfacial transition zone. All methods are indirect, because the interfacial transition zone is located between the surface of an aggregate particle and 'bulk' hardened cement paste. The methods most commonly used to date are mentioned here below.

One method of investigating the interfacial transition zone is to cast cement paste against a flat (dummy) aggregate surface, debond it after a certain hydration time and study the fracture surface, using scanning electron microscopy (SEM) complimented sometimes with energy dispersive X-ray analyses (EDX) [8, 11]. Another method is to cut slices from ordinary concrete, polish them and investigate them using SEM with backscattered electron images coupled with image analysis [16]. A third method is by comparing data from cement paste samples with data from mortar samples. This way general remarks can be made, for instance, on porosity and permeability of the interfacial transition zone [1, 17]. A last method mentioned here is X-ray diffraction (XRD), which concentrates on the crystalline constituents like calcium hydroxide and ettringite. Although the latter method has been used quite often over the past two decades to investigate the interfacial transition zone, the method is not without dispute. In appendix II some additional information as well as some comments are added.

Width of the interfacial transition zone

Often, it is said that the width of the interfacial transition zone in plain Portland cement concrete is, on average, between 40 and 50 μm. However, depending on the technique and the parameters chosen, it might not be that average. The work of Grandet and Ollivier [18, 19] made the XRD technique a common way to study the width of the interfacial transition zone. They have found that the interfacial transition zone is about 40 μm wide. On the other hand, Zimbelmann using SEM has determined the width to be about 25 μm [11].

Using backscattered electron images and image analyses, Diamond and Huang [20], concluded in 1998 that no single width can be determined for the interfacial transition zone. If the deficiency in unhydrated cement content is taken, the width extends to about 50 μm. Analysing the excess pore space, the interfacial transition zone reaches a 'bulk'-value at about 30 μm from the aggregate surface. According to the excess amount of calcium hydroxide measured with this technique, the width is only 10-20 μm.

In relation to the width, it is noteworthy to mention that Diamond et al. [21] reported that in conventional concrete the estimated average spacing between the surfaces of neighbouring aggregate particles is about 75 to 150 μm. In these paste ribbons, the interfacial transition zone appears twice!
2.2. Current explanations for the formation

The interfacial transition zone is part of the hydrated cement paste. During hydration cement reacts with water to form C-S-H gel, either by a topochemical mechanism [22], or by a dissolution-precipitation mechanism [23], or maybe both. It is very difficult to determine which mechanism has occurred [24], but the result is roughly the same: the reaction product grows from the original cement particles, much like gradually thickening shells, which interlock with adjacent grains. The formation of portlandite is a pure dissolution-precipitation mechanism. Due to the high mobility of calcium in cement paste, portlandite can form at greater distances from the original cement grains.

The microstructural characteristics of the interfacial transition zone include high porosity, long ettringite needles and a high amount of relatively large calcium hydroxide crystals. To understand these characteristics in view of the hydration process explained above, the generally accepted idea for the formation of the interfacial transition zone is, that at the onset of hardening the region close to the aggregate surface has on average less cement grains, and is rather filled with water.

Most researchers agree on this point, so the explanation for the formation of the interfacial transition zone has focussed on an explanation for the existence of a water-rich zone or increased water/cement ratio near the aggregate particle surfaces. Three major hypotheses have been put forward:

- Maso [25] and Zimbelman [26] suggest the formation of a film of water on the surface of all solid particles during mixing. This film of water (about 20 μm thick [26]) inhibits the cement grains from coming into contact with the aggregate particle surface.
- Diamond [13] points out that fresh cement paste ordinarily is flocculated and consists of multi-particle flocks that are often up to several hundred of microns in extend. These flocks pack poorly against aggregate particle surfaces, resulting in extensive areas of high local water content near the aggregate particle surfaces.
- Berger et al. [27] first mentioned the so called ‘wall-effect’, that relates to cement particles packing less efficiently at an interface than in the bulk.

An additional effect to the size of the interfacial transition zone can be caused by localized bleeding, noted by Scrivener and Pratt [28]. Water accumulates beneath the larger aggregate particles as segregation occurs due to gravitational forces.

In the previous hypotheses a few misconceptions occur. The water film idea has against it that the Brownian motion of the cement particles will not stand a water area of 40 μm wide. From a volume fraction point of view it can very easily be shown that multi-particle flocks do not occur in fresh cement paste. In fact, cement paste is one giant flock or network. As for the wall-effect, this does occur and is a known principle near surfaces. However, the size of this effect cannot explain a width of 50 μm of the interfacial transition zone, as is shown in appendix I in more detail.

Therefore, it must be concluded that the appearance of a water-rich zone near the surface of an aggregate is still not completely clarified.
2.3. An additional hypothesis for the formation

In this thesis an additional hypothesis is proposed for the formation of the interfacial transition zone. As with the hypotheses in the previous section, the problem is reduced to the explanation of the existence of a water-rich zone near the surface of the aggregates. The existence of a wall-effect is taken as a baseline in the entire process, but cannot explain the complete interfacial transition zone.

The hypothesis proposed here is based on a phenomenon known from colloid science, called syneresis. Syneresis is the contraction of a fresh gel network under the expulsion of its liquid, while the total volume of the system remains constant. The theory behind this process is explained in the next chapter.

When syneresis occurs in cement paste, liquid has to accumulate somewhere, by definition of the syneresis process. It could be that the cement paste makes way for the liquid within the paste itself. Syneresis thus might be at the origin of the larger pores in the hardened cement paste. However, it is more likely that the liquid accumulates at the rim of the cement paste, i.e. at the surface of the aggregate particles. This would even be more likely, if the aggregates are considered to be part of a rigid skeleton that can not move anymore after casting, and the cement paste could shrink away from the rigid framework. It must be noted though, that the skeleton idea for concrete is still subject to debate.

In any case, water has to accumulate somewhere. The hypothesis proposed here is that the region near the surface of the aggregate is for the moment the most likely place where the water accumulates. Thus syneresis might provide the necessary addition to the wall-effect to explain the rather large width of the interfacial transition zone. Furthermore, through the syneresis model the chemical effects are introduced in the formation mechanism of the interfacial transition zone. This is important in order to be able to explain the effect of chemical admixtures on the interfacial transition zone.

Although the main focus in this thesis is on the syneresis process itself, it has to be taken into account that the existence of the interfacial transition zone triggered the idea of syneresis in cement paste. Therefore, the possible contribution of syneresis to the formation of this zone is an important aspect of the present investigation.
Chapter 3

Flocculation and Syneresis

Red blood runs over our skin just after we have cut ourselves. Minutes later yellow blood serum tells us the bleeding has stopped. Going from red blood to a blood clot and yellow blood serum involves a common example of syneresis. Syneresis is defined as the contraction of the network in a particulate gel of solid particles, under the expulsion of its liquid, while the total volume of the system remains constant.

Syneresis is part of a complete process, particularly with a definite time scale. When blood is exposed to air, a complex system of reactions turn albumins into a network of fibrin fibers. Into this network platelets are trapped which become a fundamental part of the network. They initiate a contraction of the network to about half its original volume, under the expulsion of blood serum. The blood clot will become more and more solid, the blood flow will be stopped and the healing process can start. So, first there is the formation of a network (seconds), then the contraction while the network is still flexible (minutes) and finally the healing process (days). Usually, the differences between the subsequent time scales are several orders of magnitude.

In cement paste hydration, the occurrence of flocculation is generally accepted. In this investigation, syneresis is introduced as an additional step following flocculation. Both phenomena occur before the system has set. In the following sections flocculation and syneresis are discussed in more detail.

3.1. Flocculation

* Total potential energy of interaction

When a large number of small particles can move freely in a fluid due to their Brownian motion, particles are colliding with one another frequently. On collision, the particles may be so attracted to one another that they remain stuck together, forming a growing flock. The process of growing flocks is called flocculation or coagulation. The mechanism behind flocculation can be explained by the DLVO theory (named after the four
contributors: Derjarguin, Landau, Verwey and Overbeek). This theory is based on the interaction forces between particles in a suspension. A brief explanation is given below.

To set the stage, consider one particle set in the centre of a coordinate system and a second particle that nears the first one. The interaction forces, or more correctly the total potential energy of interaction ($V_I$) between these two particles consists of an attractive potential energy ($V_A$) and a repulsive potential energy ($V_R$); these two energies work independently and at the same time ($V_I = V_A + V_R$). The attractive potential energy is based on the long-range Van der Waals forces. The repulsive potential energy has its origin in an electric double layer that develops near the surface of a solid particle in contact with an electrolytic solution. While $V_A$ mainly depends on the interparticle distance, $V_R$ is also affected by the surface potential energy of the solid and by the electrolyte concentration (see figure 2, ref. [29]). In order for flocculation to occur, the attractive potential energy has to be greater than the repulsive potential energy.

![Graph: Potential energy of interaction vs. interparticle distance](image)

*Figure 2. Example of the influence of the electrolyte concentration ($\kappa$) on the total potential energy of interaction ($V_I$); $s$ is the centre to centre distance between particles given in particle radius. (ref. [29])*
Figure 3. Example of a change of porewater composition in a hardened Portland cement paste as a function of time [30].

*Composition of porewater.*

Immediately after mixing cement with water, minerals dissolve in the water. Figure 3 shows a typical development of the porewater composition in time [30]. The pH (≈12) is similar to that of a saturated lime solution. During the first 6 hours the composition of the porewater remains rather constant. This is the so-called dormant period in which the concrete is workable; it can be transported and cast. It is generally accepted that this dormant period is due to the formation of a layer of the double salt ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) around the Portland clinker particles. The ettringite layer prevents further dissolving and reaction of the clinker particles. In the cement mill gypsum (CaSO₄·2H₂O) or anhydrite (CaSO₄) is added as a setting-time regulator to provide the calcium sulphate for the ettringite formation.

After the dormant period, the ettringite layer is broken up and converted to so called

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Figure 4. Schematic representation of the protonation - dissolution process at the surface of a tricalcium silicate grain during the first (ten) minutes. (After Nonat and Mutin [31].)
monosulphate (3CaO·Al₂O₃·CaSO₄·13H₂O). Clinker particles restart dissolving and reacting, and the composition of the porewater shows a dramatical change; lime ions are almost disappearing, while the potassium and sodium ion concentration steeply increases, with a concurrent increase in alkalinity. For the subject of this thesis the dormant period is of special interest and in this period the porewater composition is rather constant and rich on lime ions.

For a tricalcium silicate grain, which is the main component of Portland cement clinker, Nonat and Mutin [31] have proposed a protonation and dissolution mechanism (see figure 4). It shows that the H₂SiO₄⁺ ions determine the surface charge, which should be negative, as has been reported in literature many times [e.g. 32, 33]. However, the presence of Ca²⁺ ions in the solution has a dramatic effect on the zeta potential (ζ) and on the counterion distribution at the negatively charged surface. This effect leads to a substantial change in the total potential energy of interaction between grain particles and, as follows from the DLVO theory, flocculation conditions are quickly obtained. It is generally considered that flocculation may occur when |ζ| < 25 mV [34].

* Flocculation in cement paste

The physico-chemical parameters determining the flocculation process in cement suspensions have been studied extensively by the group of Jiang, Mutin, Damidot and Nonat. Some important conclusions of their work [35, 36, 37] are mentioned in the following paragraphs.

Jiang et al. first showed that flocculation does not appear in suspensions of cement dispersed in pure alcohol. Furthermore, their micro calorimetry and conductivity measurements revealed that neither dissolution nor hydration occurred in such systems. In pure water, cement particles do flocculate. Therefore, their first conclusion was, that an aqueous ionic solution is necessary to induce flocculation.

During subsequent flocculation experiments with silica-rich Portland cement particles (CEM I) in water (w/c = 300), they noticed that calcium concentration rises rapidly up to 6 mmol/l, and the amount of hydrates reached more than 20% in the first minutes. Similar experiments in a saturated lime solution ([CaO] = 22 mmol/l) again led to flocculation, but this time there was practically no C-S-H formed (< 0.1%) during the first two hours. On the other hand, in silicate solutions in which the calcium concentration is very low, the percentage of precipitated C-S-H reached about 3% without any flocculation of particles. Therefore, they concluded that hydrate formation is not a necessary condition for the occurrence of cement particle flocculation.

In all their experiments, the calcium concentration seemed to be a very important parameter for flocculation. To increase the concentration of calcium to values above the super solubility of portlandite, they used calcium chloride (CaCl₂) solutions. They found that flocculation of cement particles is more difficult when the CaCl₂ concentration is high. Using NaCl solutions they found that the difficulty in flocculation is due to the calcium ions and not due to the chloride ions.

According to equilibrium solubility limits of CaO and SiO₂ determined in studies of the system CaO-SiO₂-H₂O, the calcium concentration can be lowered by increasing the
silica concentration. They found that flocculation between cement particles becomes less with increasing silicate concentration; the suspension remains completely dispersed when the initial silicate concentration reaches 30 mmol/l.

In their experiments, the size of the particle flocks has been studied. When the value of the median particle diameter (D_{50}) of the agglomerates, measured ten minutes after preparation of the suspension, is plotted versus the initial calcium concentration, a bell-shape curve results as shown in figure 5. Flocculation thus only occurred when a sufficient calcium concentration was reached (> 0.1 mmol/l), and tended to be less effective if the calcium concentration was greater than 100 mmol/l. They also noted that both the low and high calcium concentrations are only obtained by addition of extra ions, respectively through sodium silicates and sodium chlorides. Although they have checked that the chloride ions do not have a dispersive effect, they are not sure whether silicate ions by themselves have an effect or not.

Nachbaur et al. [38] reported that the zeta potential increases linearly with log [CaO] near the point of zero charge, which is reached at a Ca^{2+} concentration of about 4 mmol/l (see figure 6). They further noted that the point of zero charge is displaced towards higher calcium concentrations as the sulfate concentration increases. Using the total potential energy of interaction, this is easily understood: the maximum flocculation occurs at the point of zero charge, the minimum of the repulsive potential energy. It does not provide an explanation yet for the rise in zeta potential beyond the point of zero charge. According to Stein [33] the positive zeta potential is due to the number of charges provided to the surface by ions other than Ca^{2+} through chemisorption and dissociation of surface OH groups.

During a flocculation process, as described so far, a flock may grow so large that it settles from the suspension; a sediment is then formed. On the other hand, if the system is concentrated, the volume of the sediment may be so large that it fills the total available volume, so that the flocks hardly settle at all. In this case a complete network forms.

It is known, that cement paste systems with water/cement ratios of normal practice, that means much less diluted than the experiments discussed above, show hardly any

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**Figure 5.** Variation of the median diameter of the agglomerates (D_{50}), ten minutes into the experiment, versus the initial calcium concentration in solution (ref. [35])

**Figure 6.** Zeta potential of tricalcium silicate and silicate rich clinker as a function of the (final) CaO concentration of the medium (ref. [38])

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13
bleeding, which means that the network fills almost the complete volume. Yang et al. [39] have reported that the particle size distribution in the top regiment and in the bottom regiment of the sediment are completely alike, which corresponds well to the idea of one complete network or one flock.

3.2. Syneresis in general

Thomas Graham noted in 1864 [40]: “A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid, and when it advances leads to pectization. In the gel itself the specific contraction in question, or syneresis, still proceeds, causing separation of water, with division into clot and serum.” It is the first time the term syneresis is mentioned.

Syneresis does not change the total volume of a system, but is, in essence, just a relocation of solid and liquid particles. In this thesis syneresis is defined as the contraction of the network in a particulate gel of solid particles, under the expulsion of its liquid, while the total volume of the system remains constant.

For a long time, a main theory behind the syneresis process has been the idea of reducing the huge solid-liquid interfacial area in order to lower the surface free energy. However, Scherer shows, in theory and experiments based on shrinkage rate measurements [41, 42], that only a small fraction of the surface is able to engage in rearrangements that reduce the interfacial area. Otherwise, shrinkage would have been much faster than measured in experiments. He considers syneresis in inorganic gels to be generally attributed to condensation reactions.

According to Arsem [43] a structural arrangement of ‘units’ in a gel is inherently unstable. He suggested that a condensation of the solid phase is possible on three terms: the re-orientation of units, the release of loosely combined molecules of the liquid phase, and the joining of previously non-functioning residual valencies. According to him, syneresis is due to the contraction of the solid phase caused by progressive linking and re-orientation of units on a molecular scale. However, if this was the cause of syneresis, the amount of syneresis would have risen continuously, as the aging increased, for there is no reason why re-orientation should stop after a time till it is not complete. But even in gels in which syneresis is large like blood clot or vanadium pentoxide, the whole of the solvent is never squeezed out [44].

In general terms, an explanation for the occurrence of syneresis was proposed in 1930 by Prakash and Dhar [44]. They investigated the influence of electrolyte concentration, time and temperature on the syneresis of numerous inorganic gels. They found that there is always a fixed minimum of the amount of the coagulating electrolyte necessary to give a stable gel network; any amount of electrolyte greater than that minimum amount will bring about syneresis. They further found that the amount of syneresis increases continuously with the concentration of the electrolyte. Regarding the effect of time, they found that the amount of syneresis increased with time in the beginning, but stopped later on. As for the effect of temperature, they observed that the amount of syneresis is greater at higher temperatures.

Prakash and Dhar [44] assumed that the whole phenomenon of syneresis could be
based on a hydration and agglomeration hypothesis. The addition of a flocculating electrolyte to a gel forming sol diminishes the charge on the colloidal particles, and gel elements are formed. The gel elements, owing to their residual forces which could have otherwise brought about agglomeration, rapidly entrap the whole of the remaining solvent and give thus a solid gel. When the gel has been formed, the excess of the flocculating electrolyte tends to bring about a slow but continuous agglomeration and dehydration of the particles. This agglomeration tendency is the cause of the contraction of the solid mass, which squeezes out the entrapped water as syneresis liquid.

The proposed explanation by Prakash and Dhar originated from before the introduction of the DLVO theory (around 1950). Using the DLVO theory the occurrence of syneresis in general terms can be understood. Under the conditions for a rapid flocculation of a colloidal sol (i.e. particles in a suspension) the result is a very loose network, in which most particles tend to be linked to only two or three others. The whole structure of the network is very tenuous and contains a great deal of entrapped solvent (usually water). From an energy point of view the tenuous structure is not the most favourable situation. Due to the fast flocculation, the stable energy situation has been overrun. However, flocculation can still continue, only on a slower time scale. That way, the same forces that led to flocculation in the first place, continue in a second term to rearrange the network. This is the basis for syneresis.

3.3. Syneresis model in cement paste

In section 3.1. it was presented, that upon mixing water and cement, dissolution of Ca\(^{2+}\) ions lead to conditions for rapid flocculation. Actual flocculation is prevented at first by the continuous apply of shear through mixing. However, upon casting rapid flocculation occurs (within minutes) and a complete network of (hydrating) cement particles is formed in which most particles tend to be linked to only two or three others (see figure 7a). The network may contain a substantial amount of entrapped water.

Since the composition of the pore solution hardly changes during the first hours, the

![Figure 7](image_url)

*Figure 7. 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.*
same forces that lead to flocculation in the first place continue to rearrange the network on a longer time scale (hours). Because the (hydrating) particles are entrapped in a loose network, residual attraction forces can 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 7b).

Since the network can only contract when it is still flexible, syneresis stops once the cement paste has set.

3.4. Influencing the syneresis process

The syneresis model described in the previous section, includes only water and cement. In concrete, mineral additions and chemical admixtures are often used. These additions and admixtures can influence the syneresis process. In this section the (possible) influences are discussed.

The basis is the flocculated network of (hydrating) cement particles shown in figure 7a. When part of the cement is replaced by mineral additions like fly-ash, silica fume or quartz flour, the network becomes diluted, less dense and thus more fragile. So, if the network starts to contract it would be reasonable to suspect a faster rate of contraction based upon its fragility. Furthermore, the mineral additions should be included somewhere in the network model. If the mineral additions are assumed to be inside the holes of the (hydrating) cement particles network, the mineral additions might act as physical barriers once the network starts to contract, thus decreasing the degree of syneresis.

It is known, that chemical admixtures can change the flocculation behaviour of cement suspensions. For superplasticizers, Jolicoeur et al. [45] have categorized the influences into four distinct phenomena: surface adsorption, surface charging, bonding to reactive sites and steric hindrance. Jolicoeur et al. believe steric hindrance to be the most important one. The other effects can be obtained through other chemical compounds as well, but do not result in the important fluidity effect of superplasticizers. Recently, Uchikawa et al. [46] have been able to measure the steric hindrance and they confirm the findings of Jolicoeur et al.

In terms of the syneresis model, the chemical admixtures are active in two ways. First, due to the phenomena mentioned above, the flocculation effect is counter-acted, which leads to a dispersed system. The result of this process on cement paste can simply be demonstrated by the smaller sediment volume in sedimentation experiments (see e.g. Neubauer et al. [47]).

A second way by which chemical admixtures can influence the syneresis process is through osmotic pressure. When water contains large polymer molecules, the concentration of these molecules increase upon expulsion of water. Due to the increase in concentration, the osmotic pressure starts to work more strongly against the expulsion of water; the osmotic pressure tries to keep the water inside. As a consequence of this competition between syneresis expulsion and osmotic pressure, it is expected that higher polymer concentrations should lead to a lower degree of syneresis.
In order to determine qualitatively whether or not a system is subject to syneresis, it has to be observed whether or not liquid is expelled from a contracting network. Once this has been established, the degree of syneresis has to be defined in order to be able to compare different experiments with each other. Either the amount of syneresis liquid that is expelled by the network contraction can be measured, like for example Prakash and Dhar [44] did, or, the degree of contraction of the (solid) network can be determined, like for instance Van Dijk [48] did. If it is possible to measure both the amount of expelled liquid and the degree of contraction, they should be the same.

Van Dijk tried to model the syneresis of curd. To measure the degree of syneresis, he used a cylindrical slab with a diameter of 180 mm, much larger than its 5 mm thickness. By following the contraction of the slab in a vertical plane, he created a one-dimensional syneresis system, which he could study under constant conditions. The idea of studying syneresis in just one direction is adopted here.

4.1. Development of an active thin section

During the period that syneresis might be occurring 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. The total volume can be used to distinguish between chemical shrinkage and syneresis: 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 [49]. 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 too small and thus hindering the freedom of motion of the cement particles. Therefore a ‘spacer’ is introduced. For the thickness of the spacer, a compromise has to be made between the free mobility of the particles and the suppression of bleeding. Some preliminary tests showed, that a practical thickness was 100 μm.

The complete build up of the very small flat box is shown in figure 8. This set-up is called an ‘active thin section’. By placing a fresh cement paste droplet in the hole at the centre of the spacer (see figure 8) just before the cover glass is placed, the syneresis process in the hydrating cement paste should be visible under a microscope.

Berger et al. [50, 51] 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.

4.2. 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. The first image was usually taken between five and ten minutes after first contact between water and cement.

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 at one position on the rim of the cement paste droplet. An example of what is shown on such an image is given in figure 9. The images are taken at a typical magnification of 200x. During preliminary experiments, it was noticed that the heat of the microscope

Figure 9. Example of the area of analysis obtained from the active thin section.
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.

A sequence of images is used to calculate a degree of syneresis (see section 4.4.) To calculate the degree 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.

4.3. Indication of syneresis in cement paste

To investigate the occurrence of syneresis in cement paste, the experimental set-up 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 10), there appeared to be indeed expulsion of water and contraction of cement particles. However, it can be noticed from figure 10 that the expulsion of water goes over the original rim, which was not expected.

In other experiments pastes were investigated consisting only of fly ash and water with a 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. A result is shown in figure 11: 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

![Figure 10. Expulsion of water from a cement paste droplet (w/c = 0.50). A glass slide object holder was used as the substrate holder. Time is time after first contact between water and cement.](image-url)
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 capillary 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 the ‘leakage’ problem, it was realized that the water outside the original rim of the paste droplet was the result of the competition between the surface tension of the glass and water, and the capillary forces of 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 12, 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 12a). In figure 12b and 12c the cement paste contracts, while water accumulates at the rim. In figure 12d 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. This process continues in figure 12e, until in figure 12f, all the free (visible) water has been sucked in.

On the process shown in figure 12, 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. Based on the assumption that the spacer provided a constant thickness between the slide object holder and the cover glass, the cement paste droplet should have a constant thickness, and since the original rim stayed in place this implies that the total volume did not change (no chemical shrinkage at first). All together, the process shows great similarity with the phenomenon of syneresis.

Figure 12. The process of 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 as a substrate holder.
4.4. Calculating the degree of syneresis

To be able to compare different experiments with each other, it is necessary to quantify syneresis. As stated in the beginning of this chapter, the degree of syneresis can be quantified by measuring the amount of syneresis liquid, or by determining the degree of contraction of the solid network. In this thesis the degree 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 ($\Delta r$). Using this radius reduction and the initial radius of the complete cement paste droplet ($R$), the degree of syneresis in volume percentage follows from equation (1):

\[
\text{Syneresis (vol\%)} = \frac{\pi R^2 - \pi (R - \Delta r)^2}{\pi R^2} \times 100\% = \frac{2R\Delta r - \Delta r^2}{R^2} \times 100\%
\]  

(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 on the rim of a cement paste droplet during an experiment. In figure 13 the necessary parameters for the calculation are identified.

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 12). 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 \(\mu\)m. The contracted area can be divided by the width of the image (350 \(\mu\)m) 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 ($\ell$). 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.

In appendix III an error analysis on this calculation is provided. A parameter study shows that the degree of syneresis is determined with a relative error of 17%. A statistical review of an experiment that was repeated eight times shows that the actual error is about 11% for the final degree of syneresis. This error is considered to be small enough for the moment to compare different experiments and to watch for trends. However, to rely on the currently calculated degree of syneresis as a solid textbook value would over validate the current set up. In appendix III it is shown that the accuracy of the calculated degree of syneresis is currently governed by the error in the camera of the image analyser. To reduce this error, a camera with a higher amount of pixel detection per square millimetre is necessary.

To compare the results of the various experiments, the calculated degree of syneresis is plotted versus the time into the experiment (see chapters 5 and 6). In those graphs it is found sometimes that the degree of syneresis decreases towards the end of the time scale. This decrease is due to an artificial error introduced in the calculation procedure. The degree 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 lower calculated degree of contraction, ergo, a lower degree of syneresis.
Chapter 5

Syneresis in Plain Cement Pastes

Over the past two chapters, syneresis has been introduced and the experiments indicate that syneresis (or a process that shows great similarity to it) is present in cement paste. In this chapter, the results of the active thin section measurements on plain cement pastes are presented. The results include the effect on the degree of syneresis due to change in water/cement ratio, cement particle size distribution and postponed sampling. The effects of mineral additions and chemical admixtures are discussed in chapter 6.

To compare the different experiments the calculated degree of syneresis is plotted versus time. Since most of the experiments have been performed with CEM I 32.5 R and a water/cement ratio of 0.50, this mixture has been used as a reference throughout all graphs. The reference line shown in the graphs is equal to the line of the statistical analysis (see appendix III). Although all experiments are done at least in duplicate, only one of them is shown in the graphs, to keep the graphs readable.

5.1. Effect of water/cement ratio

The first parameter that has been changed is the water/cement ratio. The cement used was CEM I 32.5 R. The results of the experiments are shown in figure 14. It can be noticed that both the initial rate of syneresis and the degree of syneresis increase with increasing amount of water.

As was shown in figure 12 in the previous chapter, syneresis liquid is first expelled from the cement paste and later on taken up again. A consequence of this process is that the water/cement ratio of the cement paste changes over time. Due to the expel of water at the rim, the water/cement ratio decreases in the area where the cement particles contract. If it is assumed that the degree of syneresis is equal to the amount of water appearing in the rim, an estimation can be made on the change of the water/cement ratio. In case of the reference cement mixture with a syneresis degree of 6 vol%, it would mean that the original water/cement ratio of 0.50 drops to a ratio of 0.46.
5.2. Effect of particle size distributions

Besides the amount of water, the grain size distribution of the cement particles can be changed in a cement paste mixture. In this way the number of neighbouring particles (coordination number) and the average pore size vary. Three CEM I cements were used of which the only difference is the cement fineness. The particle size distribution of all three cements is given in figure 15. (The grain size distributions were measured with a Sympatec Helos particle size analyzer, type RODOS SR.) The fourth line in figure 15 is produced from CEM I 52.5 R that has been ground further in the laboratory with isopropyl alcohol and a vibrating disc grinder. In table I, the Blaine values of the cements used are given.

Experiments have been carried out at a water/cement ratio of 0.50 and 0.60 using these cements. The paste mixture using the extra ground CEM I 52.5 R at a

<table>
<thead>
<tr>
<th>Cement</th>
<th>Blaine specific surface (m²/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 32.5 R</td>
<td>227</td>
</tr>
<tr>
<td>CEM I 42.5 R</td>
<td>308</td>
</tr>
<tr>
<td>CEM I 52.5 R</td>
<td>374</td>
</tr>
<tr>
<td>CEM I 52.5 R (extra ground)</td>
<td>692</td>
</tr>
</tbody>
</table>
water/cement ratio of 0.50 was too dry and has not been included in the study. The results for the experiments using cement pastes with a water/cement ratio of 0.60 are shown in figure 16. The results of the experiments using cement pastes with a water/cement ratio of 0.50 show an analogous effect. The graph with these results can
be found in appendix IV.

From figure 16 it is noted that both the initial rate of syneresis and the degree of syneresis decrease as the fineness of the cement increase at a constant water/cement ratio. The difference is most profound between cement pastes using CEM I 42.5 R and CEM I 52.5 R.

5.3. Postponed sampling

From the previous graphs on the degree of syneresis versus time, it is clear that syneresis stops occurring at a certain time, which from this study seems to be after approximately two hours. Finishing the experimental program it was thought that syneresis might not be observed if samples of paste were taken from a batch some hours after mixing; an experiment was set up with postponed sampling: a sample was taken to the thin section after one hour. Most of the syneresis should then have occurred and a much lower degree of syneresis was expected.

To set up this experiment, a much larger quantity of cement paste was prepared. About 250 g CEM I 32.5 R and 125 g water were hand mixed. The cement paste was put in an airtight container and stored at 20 °C for about an hour. After that time, a big spoon of paste was gently taken out of the container. From this amount a smaller sample was gently taken using a spatula, from which a droplet of cement paste was placed in the active thin section. During this preparation the structure in the sample of the cement paste was disturbed as little as possible. The sample was placed under the microscope approximately 70 minutes after first contact between water and cement. The results from

![Figure 17. Result of the experiment with postponed sampling (w/c = 0.50).](image-url)
this experiment are shown in figure 17.

The results show that syneresis still occurs. This can also be seen in the microscope images by the accumulation of water at the rim. The time between placing the droplet in the active thin section and the moment the water starts to break up and is being sucked back into the cement paste again is about the same for both experiments. Furthermore, it is obvious from figure 17 that the degree of syneresis occurring using postponed sampling is higher than the degree occurring using a droplet of cement paste placed on the thin section immediately after mixing.

5.4. CONCLUSIONS on the syneresis model

From the results of the syneresis experiments as shown in the previous sections, the following conclusions can be drawn.

The experiments with the water/cement ratio showed that increasing the amount of water results in larger initial rate of syneresis and a higher degree of syneresis. When the same amount of cement is used, more water actually means that the network is getting thinner; the number of contact decreases and the holes become bigger to entrap more water. This less dense and more fragile network leads to a faster contraction with more water being expelled, which is indeed found in the experiments.

When the amount of water is kept the same, but the fineness of cement is increased, a decrease in both the initial rate and the degree of syneresis is found. Upon increasing the fineness of cement, in the same mass of cement more particles are now present. But when more particles are present in a fixed volume, the network is getting denser. There are more contacts between particles and there is less open space; the holes become smaller. Through this denser network it is more difficult to contract and to expel water, which leads to a lower degree of syneresis being measured.

An anomaly at this point is the experiment with the extra ground CEM I 52.5 R cement. The extra ground cement was expected to have the lowest degree of syneresis. However, the results show that the degree of syneresis of the extra ground cement is a little above the degree of syneresis of the CEM I 52.5 R cement. This might be caused by the inadequate amount of gypsum; due to the grinding the amount of reactive surface of the cement increases considerably, while the amount of gypsum stays the same. It might be that this leads to rapid reaction and stiffening of the cement paste, which could also be the explanation why the extra ground cement with a water/cement ratio of 0.50 was too dry.

In the postponed sampling experiments it was found that syneresis did occur after the postponed sampling. From the experiments it can be learned that the initial forming network seems to be reversible for at least the first hour. Otherwise, in case of a rigid network, syneresis would not have been found anymore. Furthermore, it was found that the degree of syneresis after the postponed sampling was higher than initially. Obviously the cement paste system is not an inert system during the first few hours after mixing. The cement particles do change when cement hydration products precipitate on its surface. Further research is necessary to explain the results of the postponed sampling experiments.
Described in this chapter are the results of the active thin section measurements with mixtures containing mineral additions and chemical admixtures. As mineral additions have been added: fly ash, quartz flour and silica fume. For chemical admixtures a superplasticizer, a water soluble polymer (polyvinyl alcohol) and an air entrainer have been used. Also some ground granulated blast furnace slag cements have been tested.

It is known that additions and admixtures influence the microstructure of hardened cement paste substantially. Notably the interfacial transition zone is changed. Therefore, literature references are made to the interfacial transition zone.

6.1. Blast furnace slag cement

In the Netherlands ground granulated blast furnace slag cements (CEM III) have been widely used since many decades. The dense paste structure resulting in substantially lower permeability compared to the structure obtained by using plain Portland cement, is an advantage especially in the marine environment.

Different kinds of ground granulated blast furnace slag cements have been tested in

<p>| Table II. Characteristics of ground granulated blast furnace slag cements. |
|-----------------------------|----------------|---------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Cement</th>
<th>Producer</th>
<th>Slag (mass%)</th>
<th>Blaine (m²/kg)</th>
<th>Median particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM III/A 42.5 LA</td>
<td>CBR</td>
<td>~ 45</td>
<td>467</td>
<td>10.7</td>
</tr>
<tr>
<td>CEM III/B 32.5 HSR</td>
<td>CBR</td>
<td>~ 75</td>
<td>439</td>
<td>11.6</td>
</tr>
<tr>
<td>CEM III/C 32.5 HSR</td>
<td>CBR</td>
<td>~ 85</td>
<td>459</td>
<td>9.9</td>
</tr>
<tr>
<td>CEM III/B 42.5 LH HS</td>
<td>ENCI</td>
<td>~ 70</td>
<td>337</td>
<td>12.8</td>
</tr>
</tbody>
</table>

CBR  = CBR Cement (Belgium)
ENCI  = Eerste Nederlandse Cement Industrie N.V. (The Netherlands)
this study. The characteristics of the cements are shown in table II. The particle size distributions are given in appendix IV. All paste mixtures had a water/cement ratio of 0.50. The results of the experiments are shown in figure 18. From the experiments it is noted that the degree of syneresis for the ground granulated blast furnace slag cements investigated, is slightly larger than for ordinary Portland cement.

Carles-Giberques [52] found the influence of slag additions on the interfacial transition zone to be poor during the first days, although he stated that slag additions may act as nucleation sites leading to a more disoriented crystallisation of portlandite.

Larbi [1] investigated the development of the interfacial transition zone on blast furnace slag cement. Based on the portlandite orientation, he found that the interfacial transition zone when using blast furnace slag cement was wider after one day than the interfacial transition zone resulting from the use of ordinary Portland cement. After seven days, the size of the interfacial transition zone with blast furnace slag cement paste was found to be much smaller than in ordinary Portland cement paste.

6.2. Fly ash

The fly ash used in the experiments of this study is a German EFA-Füller fly ash from a wet-bottom powder coal power plant. Blends have been prepared with different
amounts of ash replacing part of the cement (% by mass of cement). The water/solid ratio was 0.50 for all mixtures. The particle size distribution of the fly ash used is given in appendix IV. The results for the degree of syneresis for the various percentages of fly ash substitutions are given in figure 19. From figure 19 it can be seen that the presence as well as the amount of fly ash have a negligible effect on the degree of syneresis. The initial rate of syneresis is slightly increased by using fly ash. The results of the 100% fly ash substitution experiments are not plotted in figure 19, since nothing happened (see also section 4.3).

Few results have appeared in the technical literature regarding the influence of fly ash on the size of the interfacial transition zone. Carles-Gibergues [52] studied the influence of fly ash on the microstructure of the interfacial transition zone and he concluded that fly ash does not change the microstructure of the interfacial transition zone during the first days.

Larbi [1] investigated the evolution and distribution of calcium hydroxide in three low-calcium fly ash Portland cement blends on specimens of age seven days to six months. After seven days the influence of the fly ash on the calcium hydroxide orientation in the interfacial transition zone was still negligible. However, after twenty-eight days Larbi found the thickness of the interfacial transition zone substantially reduced and the degree of orientation of the portlandite crystals at the interfacial transition zone decreased. According to Larbi, these effects are regarded to be due to the pozzolanic reaction between the fly ash and the portlandite at the interface.

![Figure 19. Degree of syneresis occurring for various amounts of fly ash substitution (% by mass of cement) with a water/solid ratio of 0.50.](image-url)
6.3. Quartz flour

The effect of an inert mineral addition in the form of a non-porous alpha quartz flour has been studied in this research. The particle size distribution of the quartz flour is given in appendix IV. In the paste mixtures cement has been substituted by different amounts of quartz (% by mass of cement). The water/solid ratio was 0.50 for all mixtures.

In figure 20 the results are shown for the experiments with quartz flour as a substitution for cement. The results show that the degree of syneresis is larger for a paste mixture with quartz flour addition than for a paste mixture without quartz flour. Furthermore, the initial rate of syneresis increases significantly by adding quartz flour. The rate seems not affected by the amount of quartz flour substitution. A 100% replacement experiment was also performed to investigate the behaviour of quartz flour by itself. It showed that this quartz flour has a tendency to contract by itself.

Larbi [1] also used this quartz flour. Based on portlandite orientation data, he found the size of the interfacial transition zone of plain cement paste mixtures similar to the size of the interfacial transition zone from mixtures in which he had replaced 20% of the cement by quartz flour. Other references to the relation between quartz flour and the interfacial transition zone have not been found.

![Figure 20. Degree of syneresis occurring for various amounts of quartz flour substitution (% by mass of cement). The water/solid ratio was 0.50.](image-url)
6.4. Silica fume

The silica fume used during the experiments of this thesis was in a powdered form. The grey pellets consisted of agglomerates of silica fume particles which should fall apart upon mixing in the cement paste mixture to particles with a mean grain size of 0.1 μm. The particle size distribution of the pellets is given in appendix IV. Cement paste mixtures were prepared with different amounts of silica fume replacing part of the cement, respectively 5%, 10% and 20% by mass of cement. The water/solid ratio was always 0.50. The results are presented in figure 21. It is stressed, that none of the mixtures presented in figure 21 had any superplasticizer added. (See also section 6.5. on the influence of superplasticizers.)

The results in figure 21 show two levels of degree of syneresis. It was found that the difference between the two levels of degree of syneresis was caused by the mixing procedure. 'Poorly' mixed pastes showed nearly no difference with the reference mixture in terms of degree of syneresis, while 'well' mixed pastes showed a significant increase. Above 5% silica fume substitution, the experiments showed a specific increase of the initial rate of syneresis when silica fume was used.

It is thought that high performance concretes owe part of their improved properties to the size reduction and densification of the interfacial transition zone. These improvements of the interfacial transition zone are attributed to both the micro filling effect and the pozzolanic reaction of silica fume particles [53, 54].

According to Vivekanandam and Patnaikuni [55] silica fume particles consume calcium hydroxide present in the interfacial transition zone and make this zone denser.

![Figure 21. Degree of syneresis occurring for different amounts of silica fume substitutions. (w/s = 0.50)](image_url)
and more uniform. From their concrete specimens of age 3 to 56 days, they found that the thickness of the interfacial transition zone for concrete containing silica fume is from the early stages of hydration much smaller than the thickness of the interfacial transition zone made with plain cement. On the other hand, the result of Larbi [1] show that at an age of 7 days the size of the interfacial transition zone with silica fume is still comparable to the size of the interfacial transition zone without silica fume. At an age of 28 days, Larbi reports a significant reduction in the size of the interfacial transition zone.

### 6.5. Influence of superplasticizer

There are some doubts whether silica fume particles deserve all the credits for reducing the interfacial transition zone, or whether the reduced size could also be due to the combined effect of silica fume and superplasticizer [13]. In section 6.4, only silica fume as addition has been used. Now, also superplasticizer is added, 1.5% by mass of the binder. The superplasticizer used in this thesis was a commercial naphthalene sulfonate based superplasticizer (OFT 3 from Tillman BV Chemische Bouwstoffen). The binder was CEM I 32.5 R with a silica fume replacement percentage by mass of cement. The water/binder ratio was always 0.50. The results are presented in figure 22. The results show that there is a substantial reduction in the degree of syneresis, with or without silica fume.

![Figure 22. Degree of syneresis occurring for cement paste mixtures containing 1.5% superplasticizer (OFT3) by mass of binder and different amounts of silica fume replacements (% by mass of cement). Water/binder ratio is 0.50.](image-url)

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6.6. Polyvinyl alcohol

Chu et al. [56] found that the presence of polyvinyl alcohol (PVA) in Portland cement paste induces changes in bond strength between aggregate and cement paste. An increase in the amount of PVA led to a decrease in the size of the interfacial transition zone and a gain in bond strength seemed to arise from suppression of the porous interfacial transition zone around aggregates and an inhibition of calcium hydroxide nucleation on the aggregate surface. Kim and Robertson [57] suggest that the changes in the interfacial transition zone seem to arise from the tendency for PVA to retard flocculation of the cement grains and to increase the efficiency of deflocculation.

Based on these reports on the influence of PVA on the interfacial transition zone, in this thesis experiments with PVA were also set up. The experiments carried out were performed using two polyvinyl alcohols (PVA). One was PVA 72.000 from Merck and the other was Airvol 805 by Air Products and Chemicals, Inc. (which was the same as the one used by Kim and Robertson [57]). Solutions of 1%, 2% and 4% PVA were prepared and used to make cement pastes with a solution/cement ratio of 0.50. The results of the experiments are presented in figure 23.

From figure 23 it can be seen that there is a clear effect of the presence of PVA on the degree of syneresis. By increasing the amount of PVA, the degree of syneresis decreases. However, compared to the reference cement paste, the amount of syneresis with a low percentage of PVA is much higher than the degree of syneresis without PVA. The initial rate of syneresis seems constant for PVA 72.000 and faster than the reference cement paste. For Airvol 805 it seems like the initial rate of syneresis depends slightly on the amount of PVA; more PVA gives a slower initial rate of syneresis.

![Figure 23. Degree of syneresis occurring for cement pastes made with solutions containing different amounts of polyvinyl alcohol. The solution/cement ratio is 0.50.](image_url)
6.7. Air entrainer

Since the chemical admixtures used so far, had a lot of influence on the results of the active thin section measurements, the effect of an air entrainer was also investigated. The air entrainer was MicroAir 100 from Master Builders PCI b.v., which was added to a cement paste mixture (w/c = 0.50) by an amount of 0.50% by mass of cement. The results of the experiments are shown in figure 24. From the results it is clear that both the initial rate of syneresis as well as the degree of syneresis increase significantly by adding air entrainer.

No literature references on the effect of air entrainers on the interfacial transition zone have been found.

Figure 24. Degree of syneresis occurring for cement paste mixtures with the addition of air entrainer of 0.50% by mass of cement. (w/c = 0.50)
6.8. CONCLUSIONS on the effects of additions and admixtures

* Regarding the syneresis model

It has been found that ground granulated blast furnace slag cements have a larger degree of syneresis that ordinary Portland cements.

From the first few sections on mineral additions, it becomes clear that most mineral additions lead to a faster initial rate of syneresis. The (hydrating) cement particle network is disturbed and becomes more fragile, because part of the cement is replaced by mineral additions. The more fragile network results in a faster initial rate of syneresis.

The small sized mineral additions like silica fume and quartz flour lead to a profound increase in degree of syneresis. Thus, the suggestion in chapter 3 that mineral additions might act as physical barriers once the network starts to contract is not correct. Probably the mineral additions are part of the (cement) particle network.

Substitution with fly ash had almost no effect on the degree of syneresis.

In the second part of this chapter the chemical admixtures have been investigated. When using a superplasticizer, it was found that the degree of syneresis drops dramatically. Superplasticizers counter-act the flocculation process. In chapter 3 it was explained that flocculation is a necessity in order to have syneresis. Without a flocculated network no syneresis can occur.

By using polyvinyl alcohol, increasing the concentration led to a decrease in degree of syneresis. This might be explained by the osmotic pressure, which increases as the polyvinyl alcohol concentration increases, and works against the water expulsion process.

By adding air entrainer, both the initial rate and the degree of syneresis increase. An explanation for this behaviour has not been found yet.

* Regarding the interfacial transition zone

Conclusion towards the interfacial transition zone, based on the results presented in this chapter are difficult to validate. However, if the degree of syneresis is assumed to be an indication for the width of the interfacial transition zone, some remarks can be made.

For ground granulated blast furnace slag cement, Larbi [1] found that the interfacial transition zone was wider after one day than the width of the interfacial transition zone resulting from the use of ordinary Portland cement. With the syneresis experiments, a higher degree of syneresis is found for ground granulated blast furnace slag cement, so that would be in agreement with the syneresis having some influence on the width of the interfacial transition zone.

Using fly ash almost no influence was found on the width of the interfacial transition zone during the first days. Again this is in good agreement with the syneresis results, since they showed almost no influence either.

Based on the syneresis experiments with quartz flour substitution a wider interfacial transition zone than for ordinary Portland cement should be expected. However, Larbi reported an equal width for the interfacial transition zone, based on portlandite
orientation data.

Like quartz flour, silica fume is expected to create a wider interfacial transition zone to start with. Unfortunately in literature, all references are made to experiments with the addition of a superplasticizer. Then, also according to the syneresis experiments, the width of the interfacial transition zone is smaller.

According to the literature, an increase in the concentration of a polyvinyl alcohol should reduce the width of the interfacial transition zone. This same trend is also found based on the syneresis experiments. However, in absolute numbers the syneresis experiments give no conclusive evidence, since most of the syneresis data with polyvinyl alcohol give a much higher degree of syneresis than for plain Portland cement.

The effect of air entrainer on the width of the interfacial transition zone is not known.
Conclusions

Ending this thesis some conclusions can be drawn. These conclusions should be considered against the objectives of this research: first, to investigate the existence of syneresis in cement paste; second, if so, to develop a model for the physico-chemical behaviour of cement paste during the first hours of hydration by which this syneresis could be explained and understood. Furthermore, it should be noted that syneresis is defined here as the contraction of the network in a particulate gel of solid particles under the expulsion of its liquid, while the total volume remains constant.

* The existence of syneresis

To study syneresis, a relatively simple microscopic technique was developed during this research, called the active thin section technique. Using this technique it was observed that an initially homogeneous cement paste droplet contracted, leaving a water-rich rim at the original edge of the cement paste droplet. This process occurred mainly within the first hour after placing the droplet in the active thin section. This behaviour is similar to a phenomenon known in colloid chemistry as syneresis.

Syneresis does not exist everywhere. For instance a paste of solely powder coal fly-ash and water does not show any contraction.

* Influencing factors on syneresis

A number of parameters, known to influence the rheology of cement paste and the microstructure of hardened cement paste, have been investigated. The following conclusions can be drawn:

- Increasing the water/cement ratio increases the degree of syneresis.
- Increasing the cement fineness decreases the degree of syneresis.
- An increase in the degree of syneresis is found in samples taken from a batch one hour
after mixing.

- Adding mineral additions results in a faster initial rate of syneresis. Silica fume and quartz flour also showed a higher degree of syneresis, as did blast furnace slag cement compared to pure Portland cement paste.
- A naphtalene sulphonate based superplasticizer caused a major reduction in the degree of syneresis.
- A water soluble polymer, polyvinyl alcohol, showed an increase in degree of syneresis at low dosage. At increasing dosage the degree of syneresis decreases.
- A vinsol resin based air entrainer doubled the degree of syneresis.

*A network model*

To explain syneresis in cement paste, syneresis is introduced as an addition to the well known flocculation behaviour of cement paste. Due to flocculation a network of (hydrating) cement particles is quickly formed upon casting. This network contains entrapped water, which is expelled upon contraction of the network.

By decreasing the water/cement ratio or increasing the cement fineness more contact points between cement particles can be expected and the holes of water within the network are smaller. Consequently an increased resistance to syneresis is likely, which is found in the experiments.

By adding mineral additions as cement replacement, the (hydrating) cement particle network is disturbed. This can results in a more fragile network, causing a faster initial rate of syneresis. When the mineral additions have a great tendency by themselves to flocculate, the degree of syneresis in mineral/cement paste systems increases notably. The amount of mineral addition appears not to have a substantial influence on the degree of syneresis.

By applying dispersion agents like the superplasticizer applied in this investigation, flocculation can be counter-acted. Consequently, if no or less flocculation occurs, it can be expected that syneresis will be less, which is indeed found in the experiments. The other chemical admixtures applied increase syneresis, indicating that the effect of these agents is fundamentally different from the effect of the superplasticizer.

*The interfacial transition zone*

The idea of syneresis in cement paste was born during a study into the effects of additions on the thickness of the interfacial transition zone. Syneresis was thought to contribute to the existence of this surprisingly thick zone.

In general, additions do cause a substantial decrease of the interfacial transition zone thickness. However, in this research the additions investigated appear to increase syneresis. A closer study of the available literature revealed that the substantial reduction of the width of the interfacial transition zone appears only to happen after the cement paste has set. At young age no decreasing effect of additions appears to be present.
*Recommendations*

Although suggested in the past, the observations of syncretic in cement paste is new for concrete. Syncretic may be a phenomenon which contributes to a number of characteristics of concrete. Therefore, the following recommendations are made:

- Expand the research to real concrete. In this thesis only cement paste has been investigated.
- Investigate the effects of syncretic on bleeding. Generally, bleeding is attributed to segregation due to gravitational forces. Syncretic could also be involved.
- The cementitious matrix in hardened concrete often shows inhomogeneities. Maybe syncretic is causing these.
- Investigate the effects of superplasticizers on the width of the interfacial transition zone. This research suggests a reduction.
- The microstructural effects on the hydrating cement paste should be investigated based on the new knowledge of syncretic. Notably the new environmental scanning electron microscope (ESEM) recently available at the department should be included in the research.
- In the theoretical description of the syncretic model, the total potential energy of interaction plays an important part. In future research it is recommended to study the influence on the surface charge and the electrolyte of cement paste systems due to various additions.
- Ground granulated blast furnace slag cement (CEM III) has a larger degree of syncretic than ordinary Portland cement (CEM I). An effect can be that CEM III paste will show larger differences in local density than a CEM I paste. It deserves attention to study this possible difference and the effect of it on the observed distinction in properties like the resistance to freeze-thaw attack between CEM III and CEM I concrete.
REFERENCES


44. Prakash, S.P. and Dhar, N.R., 'The influence of the concentration of coagulation electrolyte, time and temperature on the syneresis of some inorganic jellies', *Journal of the Indian Chemical Society*, vol. 7, pp. 417-434. (1930)


APPENDIX I.

PARTICLE PACKING NEAR A WALL

Introduction

Real often, the interfacial transition zone in concrete is explained by a phenomenon called the 'wall-effect'. Although this phenomenon has long been known [1], very few calculations have been made to check whether or not the wall-effect can really explain the large width of the interfacial transition zone. In this appendix these calculations are made using two different computer-simulation models for particle packing.

In concrete, interfacial transition zones exist between aggregates and 'bulk' cement paste. Often, it is stated that the width of this zone is on average between 40 and 50 μm. Although this size seems used as a rule of thumb, recent books on the interfacial transition zone [2, 3] seem to indicate that the width of the interfacial transition zone is probably closer to 30 μm.

To explain the existence of the interfacial transition zone, most researchers agree that the formation starts with a region close to the aggregate surface, which is low on particles and rather filled with water. To account for this empty space, currently the most reported theory is the so called 'wall-effect'. In this theory, aggregates are seen as walls, against which the cement grains must pack themselves. Because effective packing of the bulk cannot be continued near a wall (see figure I.1), empty space is introduced which approaches 100% as the wall is reached.

In this appendix, two different computer-simulation models are described, which have been used to assess the extend of the effect of particle packing against a wall: a (generally used) random sequential model and a newly developed ‘SPACE’ model. The simulations have been run for cement particle size distributions of CEM I 32.5 R, CEM I 42.5 R,

Figure I.1. Schematic illustration of the wall-effect.
and CEM I 52.5 R (see appendix IV for these particle size distributions). The models simulated a solid volume density of 40%, which is comparable to a water/cement ratio of 0.50.

**Random sequential**

The common approach to simulate particle packing is by applying so called random generators. Particles of a certain range of particles are sequentially located inside a box with a given size. Each particle is put in a random position in the box, starting with the largest particles. If a random position of a particle is chosen, it is checked if there are no overlaps with the particles that are already in the box or with the boundary. If there is an overlap a new random position is chosen. After a user-defined amount of tries the particle is neglected. The number of unsuccessful attempts increase dramatically with fractional densities exceeding 0.3 [4]. In the sequential rejection processes, the spatial positions of successfully placed particles are not influenced by the particles added later.

Diamond et al. [5] have reported that in conventional concrete the estimated average spacing between the surfaces of neighbouring aggregate particles is about 75 to 150 µm. For the simulations, therefore, a box has been chosen of 100 x 100 x 100 µm³. When the simulations are finished, the fractional density can be calculated in a chosen plane. Taking this plane perpendicular to one axis and following the axis-coordinate from one side of the box to the other, gives a result as shown in figure I.2. A wall-effect is clearly visible, but to what width does it extend?

![Figure I.2. Results of the fractional density taken in a plane perpendicular to the x-coordinate for a random sequential simulation of 40 volume% fractional density.](image_url)
Table I.I. Summary of the results of the computer simulation for particle packing for four different cements.

<table>
<thead>
<tr>
<th>Cement</th>
<th>Size of wall-effect (μm)</th>
<th>Homogeneous Distribution Distance (μm)</th>
<th>Median Particle Size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Random Sequential</td>
<td>‘SPACE’ System</td>
<td></td>
</tr>
<tr>
<td>CEM I 32.5 R</td>
<td>10.4</td>
<td>13.1</td>
<td>17.4</td>
</tr>
<tr>
<td>CEM I 42.5 R</td>
<td>7.6</td>
<td>9.9</td>
<td>12.3</td>
</tr>
<tr>
<td>CEM I 52.5 R</td>
<td>6.8</td>
<td>5.7</td>
<td>9.2</td>
</tr>
</tbody>
</table>

In the simulations, the target value was 40% volume density. However, due to the particle overlap and rejection process, the actual overall volume density is only about 38%. Due to the wall-effect a much lower amount of volume density is found near the wall. The absence of particles here, leads to an excess of particles in the bulk; the bulk volume density is larger than the overall volume density. Between the wall-area with the lower density and the bulk-area with a higher density than the mean volume density, a cross-over point can be determined (see figure I.3). This cross-over point has been used to define the width of the wall-effect. In table I.I the results are summarised.

![Graph showing volume density and cross-over points on X-coordinate](image)

*Figure I.3. Example of cross-over points on the X-coordinate for CEM I 52.5 R.*
The 'SPACE' system

At Delft University of Technology, another, more 'realistic' computer model for simulating particular materials is developed: the 'SPACE' system (Software Package for the Assessment of Compositional Evolution). This 3-D structural simulation system is based on a close similarity to the production process of the real material.

In the first stage, a random 3-D dilute distribution of the elements is generated within the boundaries of a container using the random sequential method previously described. The computer may enlarge the initial size of the container to ease the initial distribution process. Furthermore, random linear and rotational velocity factors are assigned to each element.

The second stage, a dynamic stage, is an iterative procedure where the location and orientation of all elements are changed at each time step according to a Newtonian motion model. The update of each particle at every iteration step describes the most likely motion of the particle with respect to neighbouring particles, container walls and (gravitational) forces that may act on the particle. When elements meet during this time interval, a contact model defines the effect of contact on the motion/rotation update. Higher volume densities than the initial one are achieved by slowly diminishing the size of the surrounding container during the dynamic process. The contact model will prevent particles from leaving the container.

Finally, the iteration stops when certain conditions (e.g. volume density) are reached. For more details on the 'SPACE' system see Stroeven [6, 7].

For the calculations in this appendix, the 'SPACE' system simulated an overall volume density of 40% using 20,000 particles. Because 20,000 particles could not cover the

![Graph showing volume density vs. distance from boundary for different cements](image)

*Figure 1.4. Result of the simulation with the 'SPACE' system for the three cements.*
complete grain size distribution of the given cements, about 6.5 vol% at the low end and about 1.5 vol% at the high end of the grain size distribution had to be left out. The results of the simulations are presented in figure I.4. Again, the size of the wall-effect is calculated based on the cross-over point and is presented in table I.I.

**Discussion**

The microstructural characteristics of the interfacial transition zone in plain Portland cement concrete include high porosity, long ettringite needles and a high amount of relative large calcium hydroxide crystals. Unfortunately, the widths of the interfacial transition zone is different for these different characteristics. Still, recent books on the interfacial transition zone [2, 3] indicate that the width is about 30 µm in plain Portland cement concrete.

In the previous sections, the widths of the interfacial transition zones simulated with the packing models, have been calculated with the cross-over points based on the total volume density of the simulated pack. However, the distribution of the individual particles within this pack have their own distribution. The ‘SPACE’ system is capable of analysing the volume density of particles of individual size ranges. An example of the result of such an analysis is given in figure I.5. Three different fractions have been followed: a fine fraction with particles of size 3.0-5.0 µm, a medium fraction with particles of size 5-10 µm, and a coarse fraction with particles of size 10-32 µm. As can be seen from figure I.5, a larger range due to the influence of the wall can now be found. So, if a homogeneous distribution of particles is taken as a term to define the width of the interfacial transition

![Figure I.5. Individual size range distributions of CEM I 52.5 R for a fine, medium and coarse fraction.](image)

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zone, the calculated width due to the wall-effect would be much larger. For the different cements a homogeneous distribution distance is determined, based on the three given fractions. These homogeneous distribution distances are also presented in table II.

When the homogeneous distribution distance would be taken to the extreme, theoretically the distance is determined by the radius of the largest cement particle. Again, taking the extreme, this would mean that the introduction of small particles would have no effect on the width of the interfacial transition zone. However, it is known that the width of the interfacial transition zone can be reduced by small micro fillers like silica fume [8]. The reason usually given for this effect is that the smaller particles fill up the holes in between the cement particles near the wall. This implies that the homogeneous distribution distance can not be taken as the calculated size of the wall-effect.

To be able to compare the width of the interfacial transition zone from the computer simulation with the experimentally found value, it should be noted that the experimental procedure sometimes requires sectioning of a piece of concrete. Then, it must be remembered that the measured width (M) of the interfacial transition zone only resembles the actual width (A) if the particle (sphere) is cut exactly through the centre. In all other cases the measured width is larger, see figure I.6. Therefore, a correction is needed on the found width of the interfacial transition zone. It has been shown analytically by Stroeven [9] that the correction factor is π/2. Thus, the width of the interfacial transition zone found in experiments based on sectioning should be divided by π/2 for their real values, or the calculated computer-simulation values should be multiplied by π/2 before comparison to experimental data.

A last remark not yet covered should be made on the chemical effects in cement paste. In the computer-simulation models no chemical effects have been taken into account.

Figure I.6. Difference between measured value (M) and actual value (A) of a layer by cutting through a particle (sectioning plane).
This leads to an almost optimum particle packing in the bulk, with the size of the wall-effect at its maximum. However, cement particles in cement paste have a strong tendency to flocculate. This results in a poor packing of the cement particles. In the extreme, it would be that flocculation leads to such a poor packing in the bulk, that there is no difference with the miss stacking of particles near the wall anymore. The effective size of the wall-effect would then be zero. In reality, the situation is in between these two extremes. This means that the calculated size of the wall-effect is at the most given by a simulation with no chemical forces introduced (see table I.I.), but is in real concrete probably less. Furthermore, it is known that the width of the interfacial transition zone can be reduced through the use of chemical admixtures. If, for instance, a superplasticizer is used the idea is that the tendency to flocculate is reduced, which leads to a better packing of the cement particles and to a reduction in the width of the interfacial transition zone.

**Conclusions**

In this appendix it an effort is made to answer the question whether or not the existence of the interfacial transition zone can be attributed solely to the wall-effect. Therefore, two different computer simulation models for particle packing have been used to calculate the size of the wall-effect. The results of the investigations are summarised in table I.I.

The results show that the size of the wall-effect is small. For the reference cement in this thesis, CEM 132.5 R with a median particle diameter of 17.2 µm, the size of the wall-effect is calculated to be 10.4 µm by the random sequential model and 13.4 µm by the ‘SPACE’ system. In the discussion it was shown that these results should be corrected (multiplied by a factor π/2) for comparison with experimental data based on plane (sectioned) pieces of concrete. The values then become 16.3 µm and 21.0 µm respectively. Furthermore, it was shown that the introduction of chemical effects in the model would lead to a decrease in the calculated size of the wall-effect based on the simulations.

Since the width of the interfacial transition zone based on experiments is currently taken to be about 30 µm, the wall-effect can not solely explain the relatively large width of the interfacial transition zone. There has to be an additional process. In this thesis the hypothesis is made that this process could be syneresis.

**Acknowledgements**

For this appendix the help of Erik Schlangen is greatly appreciated, who run the random sequential simulations. Also much gratitude is obliged to Martijn Stroeven, who developed the ‘SPACE’ system and was kind enough to run the simulations with his model. Piet Stroeven is kindly thanked for his remarks on the sectioning and the corrections made there.
References


APPENDIX II.

XRD-MEASUREMENTS TO DETERMINE
THE WIDTH OF THE INTERFACIAL TRANSITION ZONE

Introduction

On the seventh international congress on the chemistry of cement, in 1980, Grandet and Ollivier [1, 2] presented a new method for the study of cement paste-aggregate interfaces. The method involves casting cement paste onto a piece of rock. After hardening the cement paste and the rock are separated and the debonded part is analysed by X-ray diffraction (XRD). The characteristic portlandite orientation in the interfacial transition zone is used to get an indication of the width of the interfacial transition zone. However, the method is not without dispute.

In this appendix the portlandite orientation index and the technique of Grandet and Ollivier are explained and commented. Then the technique is used to study the influence of different particle size distributions of cement on the width of the interfacial transition zone.

Portlandite orientation index

Portlandite (Ca(OH)$_2$) has a hexagonal crystal structure (see figure II.1). It can be found in the interfacial transition zone at different locations with different orientations.

In Barnes' duplex film [3] portlandite is reported with its c-axis preferentially oriented normal to the aggregate surface. In the contact layer of Zimbelmann [4] the c-axis of portlandite is parallel to the aggregate surface. Both layers are only 1-2 μm thick. Relatively large portlandite crystals are found beyond these thin layers. These crystals have their c-axis mostly parallel to the aggregate surface. There are also small stacked platelets of very pure portlandite crystals developing as secondary deposits with their c-axis perpendicular to the aggregate surface.

Since portlandite is a crystalline material XRD can be used to study its orientation. The principle of the technique is illustrated in figure II.2. An X-ray tube provides radiation which is reflected by the crystals in the specimen towards a detector. It should

![Figure II.1. Hexagonal lattice structure of portlandite with the strongest reflection planes.](Image1)

![Figure II.2. Schematic of the principle of X-ray diffraction.](Image2)
be noted that only crystals with lattice planes parallel to the specimen surface can reflect radiation towards the detector. Portlandite crystals give strong reflections on (101) and (001) at respectively 34.09 and 18.09 degrees 2-theta. When the strongest reflection (101) is set at an intensity of 100, the (001) reflection has an intensity of 74, based on a random distribution of portlandite crystals in a specimen.

Grandet and Ollivier used the intensities (I) of the peak reflections of (101) and (001) to define a portlandite orientation index (I_{CH}):

\[ I_{CH} = \frac{I_{(001)}}{I_{(101)}} / 0.74 \]  \hspace{1cm} (II.1)

If the portlandite orientation index is 1.0, there is no preferential orientation. Index values greater than 1.0 imply that there is a preferential orientation of portlandite crystals with their c-axis perpendicular to the aggregate surface.

Grandet and Ollivier quote Barnes et al. [3] to state that portlandite is formed in the interfacial transition zone in relatively large amounts with their c-axis perpendicular to the aggregate surface. They used this fact to present their portlandite orientation index as characteristic for the interfacial transition zone. However, Barnes et al. reported the existence of three portlandite morphologies with different orientations. Diamond [5] also spotted this problem. He stated that the apparent conflict is resolvable by attention to XRD theory: only the crystals that are oriented with their c-axis normal to the surface of a specimen can contribute to the enhanced basal X-ray diffraction peak; the other crystals simply do not register.

**The Grandet and Ollivier technique**

The technique proposed by Grandet and Ollivier consists of the following procedure. A cement paste is cast against a flat aggregate. Grandet and Ollivier used a plastic pipe with a diameter of 2 cm of which the aggregate formed the end piece. The aggregate-paste system is left to harden in a controlled atmosphere until a certain age. Then the specimen is demoulded and the paste is debonded from the aggregate. The aggregate side of the paste is analysed by XRD. By successive abrasion and XRD analyses a depth profile of the portlandite orientation can be obtained using the portlandite orientation index.

Although the method was presented in 1980, it was not until 1988 that remarks and comments on the new method were reported. Yuan et al. [6] pointed out by theoretical analyses that the proposed method could only be used in a qualitative method. When the method was questioned because the goniometer sweeps through only a single arc, thus missing any crystals which are not oriented with either a (001) plane or a (101) plane parallel to the interface, Detwiler et al. [7] used pole figures to confirm the validity of the portlandite orientation index.

In 1987, Zürz and Odler [8] reported the effects of hydration time, water/solid ratio and addition of melamine sulphonate or naphthalene sulphonate on the portlandite orientation index. They found that the index was not at all 1.0 for random orientation, but may change with variations of all the studied effects, with the exception of
Table II.I. Main chemical composition of Portland cement used (CEM I).

<table>
<thead>
<tr>
<th>Composition</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (%)</td>
<td>64</td>
<td>21</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Bogue</td>
<td>C₂S</td>
<td>C₂S</td>
<td>C₃A</td>
<td>C₄AF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition</td>
<td>63</td>
<td>13</td>
<td>8</td>
<td>9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

naphthalene sulphonate which had no influence.

A remark should also be made on the calculation proposed by Grandet and Ollivier. The intensity, shape and position of a diffraction peak are subject to various factors. The intensity is related to the amount of crystals, that are able to diffract. The peak can widen due to differences in crystal grain size, lattice defects or overlay from other crystals. Finally, the position of the peak can change when stresses become involved. Still, Grandet and Ollivier calculate an orientation index based on two single maximum peak point intensities. Therefore, the orientation index is a ratio of two pure count measurements. If there is a measuring error in one of those counts, or worse in both, it will immediately affect the orientation index. In other words, the measuring sensitivity is relatively high.

**Experiments**

The portlandite orientation index has been used in this thesis to determine the effect of different particle size distributions of a cement on the size of the interfacial transition zone. The cements used were CEM I 32.5 R, CEM I 42.5 R and CEM I 52.5 R. The particle size distributions of these cements are given in appendix IV. The chemical composition of the cement is given in Table II.I

Cement paste with a water/cement ratio of 0.50 were hand mixed and casted in previously prepared formwork (see figure II.3). The formwork consisted of a part of a pipe, with a perspex plate tightly fitted to the end, serving as a fake aggregate. To avoid water leakage, high vacuum grease was used between the pipe and the perspex plate.

When the cement pastes had been poured into the formwork, the system was tapped

![Figure II.3. Formwork for the XRD specimen preparation.](image-url)
five times using a small mortar table tapping device and was then placed in a conditioned room (20 °C, 95% RH) to harden for 28 days. The night before the XRD measurements, the specimen to be analysed was stored in a desiccator filled with nitrogen gas.

The XRD measurements were performed on a Siemens D500 Goniometer. Since the reflections of (001) and (101) appear at 18.09 and 34.09 degrees 2-theta respectively, a scan range was chosen between 16.00 and 38.00 degrees 2-theta. The step size was 0.04 degrees 2-theta, the counting time was 4 seconds per step. Cu-Kα radiation was generated at 45 kV and 30 mA. The goniometer was used with a divergence slit, a scatter slit and a receiving scatter slit, all of 0.3 degrees, and a receiving slit of 0.1 degrees 2-theta. The measurements were made on a spinning specimen of which an area with a diameter of about 15 mm was analysed. At an angle of 16 degrees 2-theta the radiation penetrated the specimen about 4.0 μm, at an angle of 38 degrees 2-theta about 9.4 μm.

The first measurement was made on the fresh interface, right after splitting the perspex from the hardened cement paste. Following measurements were obtained after successive abrasion of the surface of the cement paste using SiC, P1200 paper. The distance to the original interface was calculated by keeping track of the weight losses of the sample during polishing.

Results

The results of the experiments are presented in figure II.4. The portlandite orientation index has been calculated using equation (I.1) with the peak maximum intensities, corrected for the background, like Grandet and Ollivier did. Using figure II.4 an indication of the width of the interfacial transition zone can be obtained by taking that distance, at which the portlandite orientation index seriously is deviating from its bulk value. These widths are presented in table II.II.

Considering the relatively high sensitivity of the calculation method of Grandet and Ollivier, the portlandite orientation index has also been calculated using the integrated net areas of the (001) and (101) reflections. The possible problems due to background, peak broadening and peak shift are then eliminated. The result of this exercise is also presented in table II.II.

Grandet and Ollivier found the size of the interfacial transition zone to be 40 μm. Larbi [9] found the size of the interfacial transition to vary between 30 and 50 μm for ordinary Portland cement. Both values are greater than the value found in this study.

Table II.II. Results for the width of the interfacial transition zone based on the portlandite orientation.

<table>
<thead>
<tr>
<th>Cement</th>
<th>Peak maxima (μm)</th>
<th>Net integrated area (μm)</th>
<th>Added integrated area (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 32.5 R</td>
<td>13.1</td>
<td>12.9</td>
<td>13.1</td>
</tr>
<tr>
<td>CEM I 42.5 R</td>
<td>9.8</td>
<td>8.2</td>
<td>7.3</td>
</tr>
<tr>
<td>CEM I 52.5 R</td>
<td>5.7</td>
<td>6.0</td>
<td>5.7</td>
</tr>
</tbody>
</table>
Figure II.4. Portlandite orientation index ($I_{\text{orientation}}$) as a function of distance from the aggregate surface for cement with different grain size distributions, indicated here by the median particle size. (28 days old, w/c = 0.50).

Using quantitative image analysis on backscattered electron images, Scrivener and Pratt [10] reported on a gradient difference in the amount of portlandite in the interfacial transition zone. This gradient levels out to a bulk value at about 13 µm from the aggregate surface. Using the same method, Diamond and Huang [11] also reported the

Figure II.5. Same experiment as shown in figure II.4, now presented as relative amount of portlandite versus distance to the aggregate surface.
amount of portlandite only to vary at a width of 20 μm from the aggregate surface.

When the integrated net areas of the (001) and (101) reflections are added to each other, some kind of relative amount of portlandite can be plotted against the distance to the surface of the aggregate (see figure II.5). A distance can be calculated at which the relative amount of portlandite starts to deviate from the bulk level value. This distance can also be used to define a width of the interfacial transition zone. The results are presented in table II.II. For normal cement (CEM I 32.5 R) the value does agree with the size found by the image analysis technique.

It is noted here, that the size of the gradient in portlandite found in this research is comparable to the size of the wall-effect. The size of the wall-effect is explained in appendix I.

Conclusions

In this appendix a technique is discussed proposed by Grandet and Ollivier to obtain an indication for the width of the interfacial transition zone using XRD measurements. It is noted that the method only examines part of the portlandite present in the interfacial transition zone. Furthermore, the portlandite orientation index is defined to be 1.0 for random orientation. Zürz and Odler [8] state that this is not always true in bulk cement paste. Finally, it is noted that the technique might be very sensible to measuring errors.

The portlandite orientation index has been used in this research to study the effect of particle size distributions of cement on the width of the interfacial transition zone. It was found that the width decreases with decreasing size of the cement grains.

Acknowledgements

The XRD experiments have been performed at the Laboratory of Materials Science in Delft. The discussions with Mr. Van der Pers have been greatly appreciated. Mr. Van Lent is thanked very much for performing the experiments.

References


APPENDIX III.

ACCURACY ANALYSIS ON SYNERESIS CALCULATION

Introduction

Of course any amount of syneresis that is determined contains a certain error. In this appendix a review is given on the calculated amount of syneresis in relation to its accuracy.

It should be noted first that the technique of using an active thin section requires a reasonable amount of experience and skills from the researcher (as real thin sections do too). Only a small amount (a few grams) of paste is prepared which is hand-mixed. A droplet of this mixture is placed within the thin section build-up. Next, a spot at the rim of the cement paste droplet is chosen to follow the experiment. All these actions are judgement calls by the researcher: when is the paste homogeneous? Is the water/cement ratio in the droplet equal to the water/cement ratio of the paste mixture? Is the spot chosen to follow the measurements comparative to the entire droplet reaction?

Furthermore, there are some aspects which do have an influence on the process inside the active thin section, but are difficult to get a grip on. For instance, the microscope light produces some heat changes inside the active thin section. Although the heat influence can be shown to exist, it is very difficult to quantify it. Also, for the same reason, the heat influence due to the reactions of the hydrating cement paste is uncertain.

On the other hand, not all these uncertain parameters are out of reach. The spot position can be checked after the experiment. If it turns out to be not comparative, the results are disregarded. An example of a wrong spot choice is shown in figure III.1.

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Figure III.1. Example of spot choice problems, here at a ‘sharp’ corner of the cement disc.
Parameter study

With $R$ being the radius of the original cement disc and $\Delta r$ being the reduction of this radius due to syneresis, the amount of syneresis ($S$) can be calculated by (see chapter 4):

$$S = \frac{2R \Delta r - \Delta r^2}{R^2} \quad \text{(III.1)}$$

Then, for the accuracy in $S$ it can be derived that:

$$\left(\delta S\right)^2 = \left(\frac{2R \Delta r^2 - \Delta r^2}{R^4}\right)^2 \left(\delta R\right)^2 + \left(\frac{2R^3 - 2\Delta r R^2}{R^4}\right)^2 \left(\delta \Delta r\right)^2 \quad \text{(III.2)}$$

Since the accuracy of $S$ depends on the accuracy of the radius $R$ and the accuracy of the radius reduction $\Delta r$, these parameters are studied successively.

First the accuracy in $R$. Since

$$R = \sqrt{\frac{O}{\pi}} \quad \text{(III.3)}$$

this leads to

$$\left(\delta R\right)^2 = \frac{1}{4\pi O} \left(\delta O\right)^2 \quad \text{(III.4)}$$

with $O$ being the total area of the cement paste droplet. The accuracy of $O$ has been determined statistically by measuring a lot of samples more than once. The error $\delta O$ turned out to be $2.0\%$.

The calculation for the accuracy of $\Delta r$ requires the errors in the calculated image area ($A$), the width of the image ($w$) and the rimline ($\ell$), because

$$\Delta r = \frac{2A}{(w + \ell)} \quad \text{(III.5)}$$

so

$$\left(\delta \Delta r\right)^2 = \frac{4}{(w + \ell)^2} \left(\delta A\right)^2 + \frac{4A^2}{(w + \ell)^4} \left(\delta w\right)^2 + \frac{4A^2}{(w + \ell)^4} \left(\delta \ell\right)^2 \quad \text{(III.6)}$$

The accuracy of $A$ is equal to the error in the amount of selected pixels (selected by threshold value of the intensity). This is very accurate and comes down to half a squared pixel. However, this is calculated from an original image area subtracted by an interim image area. Therefore, this error is made twice, which results in a multiplication by $\sqrt{2}$. At an enlargement of 200x, one pixel equals 0.719 µm, which means the accuracy of $A$ comes down to 0.37 µm².

The width of the image can be determined very accurately as well. The error is equal
to the size of one pixel: 0.719 μm.

To measure the rimline $l$, a line has to be drawn along the rim of the cement paste droplet (only in the obtained image) by the researcher. Therefore, the accuracy of $l$ depends partly on the effort of the researcher. With one pixel still representing 0.719 μm, statistical evaluation shows that the rimline can be determined with an accuracy of 4.3 μm.

With all these values known, an example calculation can be made on the theoretical accuracy of $S$. A typical value for $R$ would be around 1500 μm; the width of the image is 350 μm; the rimline is typically around 375 μm. The amount of the calculated image area changes with time. Values for the amount of syneresis of 2 vol%, 4 vol% and 6 vol% have been calculated. Therefore, $A$ has to be respectively 5500 μm$^2$, 11000 μm$^2$ and 16600 μm$^2$, which result in absolute accuracies of $S$ of 0.3 vol%, 0.7 vol% and 1.0 vol%, or a relative accuracy of 17%.

**Statistical review**

In the previous section, the theoretical accuracy of the syneresis calculation has been derived. Another method is just to repeat the same experiment over and over again and then calculate a statistical standard deviation. This has been done eight times for CEM I 32.5 R cement and water with a water/cement ratio of 0.50. The results of these experiments are shown in figure III.2.

To use this data statistically, the results are put into groups. The time periods are given

![Figure III.2. Degree of syneresis versus time for the repeated experiment with CEM I 32.5 R cement and a water/cement ratio of 0.50. (The codes are the experiment numbers.)](image)
in table III.I. For these periods average syneresis values (avg. $S$) and the statistical deviation of these averages (std. $S$) have been calculated, which are also given in table III.I. Graphically, the results of the interpretation are shown in figure III.3.

Table III.I. Statistical parameters of repeated tests on CEM I 32.5 R
($n =$ number of data points, avg. $S =$ average degree of syneresis, std. $S =$ standard deviation on the average degree of syneresis)

<table>
<thead>
<tr>
<th>Time period (min.)</th>
<th>$n$</th>
<th>avg. $S$ (vol%)</th>
<th>std. $S$ (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 - 30</td>
<td>6</td>
<td>1.22</td>
<td>0.71</td>
</tr>
<tr>
<td>30 - 40</td>
<td>5</td>
<td>2.37</td>
<td>0.41</td>
</tr>
<tr>
<td>40 - 60</td>
<td>5</td>
<td>3.60</td>
<td>1.35</td>
</tr>
<tr>
<td>60 - 80</td>
<td>5</td>
<td>4.71</td>
<td>1.16</td>
</tr>
<tr>
<td>80 - 100</td>
<td>6</td>
<td>5.45</td>
<td>1.40</td>
</tr>
<tr>
<td>100 - 150</td>
<td>6</td>
<td>6.05</td>
<td>0.77</td>
</tr>
<tr>
<td>150 - 200</td>
<td>5</td>
<td>6.27</td>
<td>0.80</td>
</tr>
<tr>
<td>200 - 300</td>
<td>6</td>
<td>6.10</td>
<td>0.57</td>
</tr>
<tr>
<td>300 - 400</td>
<td>7</td>
<td>6.27</td>
<td>0.62</td>
</tr>
<tr>
<td>400 -</td>
<td>6</td>
<td>6.02</td>
<td>0.64</td>
</tr>
</tbody>
</table>

Figure III.3. Statistical analysis of data from figure III.2. (see also table III.I)
Conclusions

The parameter study into the accuracy of the calculated amount of syneresis shows that theoretically the amount of syneresis can be determined with a relative error of 17%. From the parameter study it follows, that the size of this error is largely due to the error in the rim line determination, or actually due to the resolution of the image analyser camera.

The statistical review of an experiment that was repeated eight times reveals that the actual error is about 11% for the total amount of syneresis. In the first part of the curves, when the syneresis is most active, a much larger difference between the results is found, probably due to the kinetics of the process.

From both the parameter study and the statistical review it is concluded that the calculated amount of syneresis (for the moment) is accurate enough to compare the different experiments and for identifying trends.

Recommendations

To increase the accuracy in the calculation of the amount of syneresis it is recommended that the error in image analysis is reduced. This means using a better camera with a higher amount of pixels detection per square millimeter. Now, the relative errors of the rim line and the width of the image are respectively 1.1% and 0.2%. If these values, for instance, both could be brought down to 0.05%, the relative accuracy in the calculated amount of syneresis would drop from 17% to 1.3%. This means that an amount of syneresis of about 6 vol% could then be calculated with an accuracy of 0.1 vol% instead of 1.0 vol%.
APPENDIX IV.

PRESENTATION OF MEASUREMENT GRAPHS

Yet most of the graphs have been presented already in this thesis, all data is collected and presented graphically in this appendix, for the reader’s convenience.

**Particle size distributions**
- Figure IV.1. Particle size distribution of Portland cements.
- Figure IV.2. Particle size distribution of granulated blast furnace slag cements.
- Figure IV.3. Particle size distribution of the different mineral admixtures used.

**Statistical analysis**
- Figure IV.4. Repeated experiment with CEM I 32.5 R.
- Figure IV.5. Statistical analysis of repeated experiment (figure IV.4.)

**Plain cement experiments**
- Figure IV.6. Results with various water/cement ratios.
- Figure IV.7. Results with different grain size distributions (w/c = 0.50).
- Figure IV.8. Results with different grain size distributions (w/c = 0.60).
- Figure IV.9. Result of the experiment with postponed sampling.

**Mineral additions**
- Figure IV.10. Results with ground granulated blast furnace slag cements.
- Figure IV.11. Results with various amounts of fly-ash substitutions.
- Figure IV.12. Results with different amounts of silica fume (no superplasticizer).
- Figure IV.13. Results with alpha quartz flour substitution.

**Chemical admixtures**
- Figure IV.14. Results with superplasticizer and silica fume.
- Figure IV.15. Results with different solutions of polyvinyl alcohol.
- Figure IV.16. Results for addition with air entrainer.
Figure IV.1. Particle size distribution of Portland cements.

Figure IV.2. Particle size distribution of ground granulated blast furnace slag cement.
Figure IV.3. Particle size distribution of the different mineral admixtures used.

Figure IV.4. Degree of syneresis versus time for the repeated experiment with CEM I 32.5 R cement and a water/cement ratio of 0.50. (The codes are the experiment numbers.)
Figure IV.5. Statistical analysis of data from figure IV. 4. (see also table III.1)

Figure IV.6. Degree of syneresis measured over time for cement pastes having different water/cement ratios. The cement used was CEM I 32.5 R.
Figure IV.7. Degree of syneresis versus time for cement pastes having a water/cement ratio of 0.50 and made of cement with different particle size distributions.

Figure IV.8. Degree of syneresis versus time for cement pastes having a water/cement ratio of 0.60 and made of cement with different particle size distributions.
Figure IV.9. Result of the experiment with postponed sampling ($w/c = 0.50$).

Figure IV.10. Degree of syneresis occurring for different ground granulated blast furnace slag cements ($w/c = 0.50$).
Figure IV.11. Degree of syneresis occurring for various amounts of fly ash substitution (% by mass of cement) with a water/cement ratio of 0.50.

Figure IV.12. Degree of syneresis occurring for different amounts of silica fume substitutions. (w/c = 0.50)
Figure IV.13. Degree of syneresis occurring for various amounts of quartz flour substitution (% by mass of cement). The water/solid ratio was 0.50.

Figure IV.14. Degree of syneresis occurring for cement paste mixtures containing 1.5% superplasticizer (OFT 3) by mass of binder and different amounts of silica fume replacements (% by mass of cement). Water/binder ratio is 0.50.
Figure IV.15. Degree of syneresis occurring for cement pastes made with solutions containing different amounts of polyvinyl alcohol. The solution/cement ratio is 0.50.

Figure IV.16. Degree of syneresis occurring for cement paste mixtures with an addition of air entrainer of 0.50% by mass of cement. ($w/c = 0.50$)
Samenvatting

Beton in z'n eenvoudigste vorm, bestaat uit een mengsel van cement, water en toeslagmateriaal. Het cement met water vormt een soort lijm die hard wordt en het toeslagmateriaal bij elkaar houdt. In de beginjaren van 1950 wordt ontdekt dat de hechting tussen het verharde cementsteen (de lijm) en de toeslagkorrels erg zwak is. Er bevindt zich een porueuze laag met een afwijkende microstructuur tussen het toeslagmateriaal en de 'bulk' structuur van het verharde cementsteen. Behalve dat het beton makkelijk breekt op deze laag, is het ook een belangrijke transportader voor zouten, waardoor de duurzaamheid van beton wordt bedreigd.

Over de oorzaak achter het ontstaan van deze zogenaamde interface zone is in de literatuur vrij snel overeenstemming. In het begin van het hydratatieproces moet een overmaat aan water aanwezig zijn geweest bij het grensvlak met het toeslagmateriaal. De belangrijkste oorzaak voor de wateroverlast wordt tot nu toe gezien in een zogenaamd 'wand-effect'. Omdat korrels hun perfecte stapeling uit de bulk niet kunnen voortzetten aan de wand, simpelweg omdat die wand daarvoor in de weg staat, is er aan het grensvlak relatief meer water dan cement in vergelijking met de bulk. Echter, bij korrels met een korrelgrootte-mediaan van ongeveer 17 µm is het moeilijk te begrijpen dat het wand-effect de interface zone met een dikte van 50 µm zou kunnen verklaren (zie ook appendix I). Er klopt dus iets niet in de verklaring. Dit was het motief voor het huidige onderzoek.

Naast een motief was er ook een startpunt. Professor Frens van de sectie Fysische Chemie uit Delft, kwam bij het promotie-onderzoek van mijn voorganger Joe Larbi in aanraking met het hierboven geschetste probleem. Vanuit zijn achtergrond kwam hij met de suggestie van synerese. Synerese is het samentrekken van het netwerk in een bepaalde gel van vaste deeltjes, waardoor de gelvloeistof wordt uitgedreven, terwijl het totale volume van het systeem niet verandert. Het doel van het onderzoek beschreven in dit proefschrift is de aanwezigheid van synerese in cementpasta's te onderzoeken en te proberen een fysisch-chemisch model te vinden waarmee synerese in cementpasta's begrepen en verklaard zou kunnen worden.

In dit proefschrift wordt een model voor het synerese proces in cementpasta's voorgesteld, dat voortborduurt op het bekende flocculatiedrag van cementdeeltjes. Wanneer water en cement gemengd worden, dan zijn het met name de Ca²⁺-ionen in de oplossing die verantwoordelijk lijken voor de snelle flocculatie (samenkitten) van cementdeeltjes. Bij het storten vormt zich zeer snel een compleet netwerk van (hydraterende) cementdeeltjes, waarbij veel deeltjes slechts aan twee of drie andere deeltjes vastzitten. In een normaal betonmengsel bevat dit netwerk een behoorlijke hoeveelheid omsloten water. Dezelfde krachten die in eerste instantie leiden tot snelle flocculatie, proberen het netwerk in een tweede termijn nog te modificeren. Dit tweede en iets langzamere flocculatieproces, waarbij de cementdeeltjes dichter naar elkaar toe bewegen, wordt synerese genoemd.

In dit proefschrift wordt gesuggereerd dat synerese de noodzakelijke aanvulling op het wand-effect zou kunnen zijn om de interface zone te verklaren, als er vanuit gegaan wordt dat de uitgedreven syneresevloeistof zich verzamelt aan het grensvlak van het
toeslagmateriaal.

Om synerese in cementpasta te kunnen aantonen is een speciaal ‘active thin section’ ontworpen. In dit zeer kleine, platte doosje kan een hydraterende cementdruppel bestudeerd worden onder de microscoop. Microscoop-opnamen aan de rand van een cementpasta-druppel, genomen oplopend in de tijd, tonen aan dat het oppervlak van het totale volume in eerste instantie niet verandert, terwijl er wel aan de rand van de cementpasta-druppel een laagje water ontstaat onder gelijktijdig krimpen van de cementpasta. De aanwezigheid van synerese in cementpasta lijkt daarmee aangetoond.

In het onderzoek zijn als variabelen meegenomen: de water/cement verhouding; de fijnheid van het cement; het effect bij een soort uitgestelde synerese-proef; de effecten bij hoogovencementen; veranderingen bij cementsubstituties door vliegas, kwartsmeel en silica fume; chemische invloeden door toevoeging van superplastificerder, polyvinyl alcohol en luchtbelvormer. Uit de onderzoeken blijkt dat veel van de waargenomen effecten heel aardig kunnen worden verklaard met het voorgestelde synerese model.

Door de water/cement verhouding te verlagen of door een fijner cement te gebruiken, wordt een groter aantal contacten tussen de cementdeeltjes gecreëerd en neemt de hoeveelheid water per holte in het netwerk af. Daaruit volgt een verhoogde weerstand tegen synerese. Door toevoeging van minerale vulstoffen wordt het netwerk van (hydraterende) cementdeeltjes verstoord. Dit resulteert in een fragieler netwerk met een hogere initiële snelheid van synerese tot gevolg. Als de minerale vulstoffen zelf ook grote neiging tot flocculatie hebben, wordt de uiteindelijke hoeveelheid synerese ook vergroot. Bij het toepassen van dispergerende middelen zoals de superplastificerder in dit onderzoek, wordt flocculatie tegengewerkt. Indien er geen of weinig flocculatie is, is synerese nauwelijks mogelijk, hetgeen inderdaad gevonden wordt in de experimenten.

Of het synerese model daadwerkelijk de benodigde aanvullende verklaring is voor het ontstaan van de interface zone, is nog moeilijk te achterhalen. Synerese treedt op in de eerste paar uur van het hydratatieproces. De gevolgen uit deze zeer korte periode op de interface zone is eigenlijk niet echt goed onderzocht. Meestal zijn de eerste waarnemingen over de interface zone pas van ver na deze periode.

Aan de andere kant is het wel een uitdaging voor de toekomst om de reikwijdte van het synerese model te onderzoeken. Juist omdat in de eerste paar uur van de hydratatie eigenlijk de fundamenten voor de microstructuur van het verhardte cementsteen wordt gelegd, kan synerese een belangrijke rol blijken te spelen bij de beïnvloeding van die uiteindelijke structuur.

Mario de Rooij,  
Maart 2000.
Persoonlijk/Dankwoord

Dit proefschrift is eigenlijk een proefschrift. Het telt in werkelijkheid circa 160 bladzijden geheel handgeschreven. Met dit lettertype heb ik geprobeerd mijn gekriebel te benaderen om zo iets persoonlijks iedereen te bedanken die mij de afgelopen jaren heeft geholpen of gesteund. Daarnaast nog een speciaal woord van dank voor een paar bijzondere mensen.

Alleen eerst mijn promotor Jan Bijen. Hoewel slechts een dag in de week aan de TV werken, zag ik je vaker dan dat collega promovendii hun volkstijds professor zagen. Als je bij collega promovendii aanschouw in hun promotiecommissie, hoorde ik vaak, dat ze van jou de meeste en de bruikbaarste commenaraan hielden. Ik puijs mijzelf dan ook gelukkig dat jij mijn promotor was.

Professor Frans, beste Gent. Hoewel u mijn tweede promotor was, ben ik nog steeds niet zeker van de woordzaam. Het geeft voor mij precies het gestijpelen aan tussen de plezierige samenwerking en de eenbiedige afstand. Ik waardeerde het feit dat je me midden in mijn twijfels niet iets langzamerhand te proberen en zo onzekerheden weg te nemen. Het proefschrift was het en zonder jou zeker niet in de huidige vorm gekomen.

Humor is voor mij belangrijk. Met mijn naaste collega Hans Janssen heb ik gelukkig heel veel gelachen. Verder zal ik onze discussies voor het board niet snel vergeten. Ik heb veel ideeën op je uitgeprobeer en ik waarderde je respon.

Bovendien humor, ik trouw (la lot) om one of those trips met Kalliopi Aligizaki. This now very special friend turned into her alter ego, a little Devil, when she started correcting my English. Although she even pointed out errors in my French references titles, her Greek-American could not always convince my British-English. Still, I would like to thank her very much for all her careful checking and showing me what civil engineers do know it.

Verder wil ik als laatste nog mijn vader en moeder in dit dankwoord betrekken. Zij hebben mij de mogelijkheid gegeven om te studeren. Ik hoop dat ik van dit dankwoord en daar te promoveren iets terug doe voor al hun ondersteuning.
Curriculum vitae

1969 Born in Alkmaar on February 6th.


1995-1999 Ph.D. student in the Materials Science group of the Civil Engineering Department of Delft University of Technology.

1999 - Post-Doctoral position in the new Micromechanical Laboratory of the Civil Engineering and Geoscience Department of Delft University of Technology.
That's all!