

AN EVALUATION OF METHODS FOR MEASURING CHEMICAL SHRINKAGE OF CEMENTITIOUS PASTES



Harald Justnes,
Dr. Ing., Senior Research Engineer,
SINTEF Structures and Concrete,
N-7034 Trondheim, NORWAY,
Tel: +47-73 59 69 22, Fax: +47-73 59 71 36,
E-mail: harald.justnes@kobe.sintef.no

Bert Reyniers, M. Sc. and
Dirk Van Loo, M. Sc.,
Katholieke Universiteit te Leuven,
Faculteit Toegepaste Wetenschappen,
Departement Burgerlijke Bouwkunde,
B-3001 Heverlee, BELGIUM

Erik J. Sellevold,
Ph.D., Professor,
Department of Structural Engineering,
The Norwegian Institute of Technology (NTH),
The University of Trondheim (UNIT),
N-7034 Trondheim, NORWAY

Abstract

In order to overcome the increased cracking tendency of high performance concrete applied in practice (e.g. bridge decks), a better understanding of the fundamental process in the equivalent binder must be obtained. Thus, two methods for measuring chemical shrinkage of cement paste have been evaluated: The dilatometry technique for total chemical shrinkage measurement based on 1) putting the paste in a recipient (e.g. Erlenmeyer flask), 2) filling the rest of the recipient with water, 3) plugging the recipient with a stopper with a water filled pipette stuck through and 4) following the total volume change by reading the fall of the water level in the pipette versus time. The elastic bag (i.e. condom) method for measurement of external chemical shrinkage based on Archimedes principle (the external shrinkage of cement paste filled in an elastic rubber bag will lead to a reduction in buoyancy, which will be directly measured as a weight increase under water).

Erlenmeyer flasks are recommended as recipients to the usual tubes in the total chemical shrinkage test, since recipients with a larger diameter has the advantage of increasing the surface-to-volume ratio of the paste. A greater mass of cement paste will also lead to higher accuracy. The paste thickness and the excess water phase do not seem to affect the measurement of total chemical shrinkage the first 48 h, with the exception of a minor difference in the period 3-12 h.

The optimum mass of the sample enclosed in an ordinary condom as elastic bag for the external chemical shrinkage, is between 300 and 450 g. Entrained air in the paste and entrapped air in the condom must be avoided since that will also lead to the detection of a erroneously high external chemical shrinkage. The true external chemical shrinkage can only be measured for stable cement pastes, since bleeding will lead to erroneously high values. If no stabilizing additives or admixtures are added, the true external chemical shrinkage of cement paste with w/c ranging from 0.35 upwards can only be measured by continuous rotation of the sample interrupted by the weighing.

Key words: Chemical shrinkage, external, total, cement paste

1. INTRODUCTION

High performance concrete (HPC), meaning concrete with $w/c \leq 0.4$, is used more and more frequently in Norway today in order to obtain durable concrete structures in aggressive environment. However, when using HPC for in particular horizontal surfaces (e.g. bridge decks), an increased sensitivity to cracking at early ages (< 12 h) has been observed. In order to overcome this problem, a better understanding of the fundamental process in the binders for HPC is required. Thus, two methods for measuring chemical shrinkage of cement paste have been evaluated in the present paper.

The total chemical shrinkage during the hydration of cement is caused by the smaller volume of products (e.g. CSH gel and CH) compared with the reactants (e.g. alite and water). As a rule of thumb, the total chemical shrinkage at 100 % hydration is about 6.25 ml/100 g cement (i.e. 25 % of the chemical bound water corresponding to a w_n of 0.25) /1/. The total chemical shrinkage equals the external chemical shrinkage until the net-work of hydration products bridging the unreacted cement grains is strong enough to resist the contracting forces. At this point (5-9 h depending on cement composition, fineness, w/c etc.), the external chemical shrinkage rate slows down drastically and the shrinkage vs time curve flattens out. Thereafter, the second manifestation of total chemical shrinkage; the formation of internal contraction pores, is dominating.

The terminology in the present paper is total chemical shrinkage, which is the sum of external chemical shrinkage and the volume of empty contraction pores at all stages. In literature, there is a terminology confusion: Total chemical shrinkage may be named *water absorption*, *volume contraction*, *autogenous volume change* or *Le Chatelier shrinkage* after the first scientist who examined the shrinkage of cement paste. External chemical shrinkage is also named *external volume change*, *bulk shrinkage* and *autogenous shrinkage*.

The methods for measuring total chemical shrinkage all have in common that the sample has to be kept water saturated and that the water needed to replace the volume decrease is measured, while the common methods for measurement of external chemical shrinkage are characterized by sealed curing of the cement paste. There are mainly three techniques for measuring chemical shrinkage; 1) dilatometry, 2) gravimetry and 3) pycnometry.

Dilatometry is based on direct measurements of length or volume change.

The most common dilatometry technique for total chemical shrinkage measurement is to put the paste in a recipient (e.g. glass tube), filling the rest of the recipient with water and plugging the recipient with a stopper with a water filled pipette stuck through. Reading the fall of the water level in the pipette versus time gives the total volume change. Knudsen and Geiker /2/ have pioneered a variety of applications for this method since the 1980's. The practical arrangement of this technique is also evaluated in the present paper.

A dilatometry technique for external shrinkage measurement has been utilized by measuring the uniaxial length change of a flexible, sealed tube by inductive sensors /3/.

Gravimetry is based on indirect measurement of volume change by recording reduced buoyancy under water by weighing (i.e. the law of Archimedes). If the weight change of a container filled with paste and excess water having at least one flexible wall is recorded, the total chemical shrinkage is measured /4/. If the weight change of a sealed elastic bag filled with paste only is registered, the external chemical shrinkage is measured. The latter method is evaluated in the present paper.

Pycnometry is only applicable for total chemical shrinkage measurements, and is carried out by filling a pycnometer with paste and topping it with water. Water is added to refill the pycnometer at different ages, and the weight increase relates to the total volume change.

2. EXPERIMENTAL

2.1 Chemicals

The testing of the methods was performed with an ordinary Portland cement (P30) from Norcem A/S, Brevik, Norway, with the chemical composition; 63.16 % CaO, 20.28 % SiO₂, 3.61 % Fe₂O₃, 4.89 % Al₂O₃, 2.98 % SO₃, 2.21 % MgO, 1.26 % free lime, 1.15 % K₂O and 0.37 % Na₂O, corresponding to the potential minerals 57.0 % C₃S, 16.0 % C₂S, 6.9 % C₃A and 11.0 % C₄AF according to Bogue calculations. The specific surface according to Blaine was 309 m²/kg. The water was distilled before use.

Precipitated calcium carbonate, CaCO₃, laboratory grade (>96 % pure) was delivered by KEBO Lab A/S, Trondheim, Norway. The specific surface was measured to 18 m²/g by nitrogen adsorption (BET).

2.2 Methods

2.2.1 Mixing procedure

Cement and water was blended in a Hobart mixer of 5 l capacity. The mixing times were 2 min at gear 1 and 1 min at gear 2. The bowl with paste was put on a vibrating table to remove most of the entrained air. The starting time of the experiments was the first contact

between cement and water (time = 0), and the first measurements started at 1 h.

2.2.2 Total chemical shrinkage

Cement paste was put into three recipients (e.g. tubes or flasks) for parallel experiments. The weights of the empty and filled recipients were measured in order to determine the amount of paste. The recipients were then carefully filled with distilled water at room temperature in a manner to avoid turbulence. A silicon rubber stopper was used to plug each recipient, taking care not to enclose any air bubbles. A pipette was filled with water and stuck through a hole in the stopper. A graded pipette of 0.2, 0.5 or 1 ml was chosen depending on the expected volume change. The recipients were put in a water bath at $20\pm 1^\circ\text{C}$. Every hour until 48 h, the position of the meniscus in the pipettes was read. The decrease of the water column in ml is directly the total chemical shrinkage (as a drop of liquid paraffine on top prevented evaporation), which were expressed as ml/100 g cement after a calculation of the mean value from the three parallel measurements. The method rely on the assumption that all contraction pores are filled with water.

2.2.3 External chemical shrinkage

Three condoms (i.e. elastic rubber bags) were unrolled partly and filled with cement paste while unrolling further in order to avoid the enclosure of air bubbles. Each condom was then twisted on the top part below the paste level, and a thin copper wire was tied around the twisted part. The slurry was rinsed out of the top part with water at room temperature. The condom was wiped dry, and silicon glue was sprayed into the open end as a sealant. The excess end part was cut off and the total mass determined.

The filled condoms were kept in a water bath of $20\pm 1^\circ\text{C}$. During the first 10 h, the condom was weighed every hour under water. Relying on Archimedes principle, an external shrinkage will lead to a reduction in buoyancy, which will be registered as a weight increase. For weighing, the condom was placed in a basket under water hanging on a scale. Prior to reading the weight under water, all air bubbles were carefully removed from the outside of the condom. After weighing, the sample was placed back into the water bath in identical orientation as before weighing in order not to disturb the fragil skeleton and/or the "bleeding" effect.

The last weighing under water was performed at 48 h. Then the condoms were wiped dry and weighed in air. Finally, the condom was stripped off and weighed including copper wire and silicon glue in order to calculate the net weight of the cement paste. The external shrinkage is presented as the mean value of three parallel measurements and given in ml/100 g cement.

3. RESULTS AND DISCUSSION

3.1 Total chemical shrinkage

3.1.1 Effect of the recipient

A few different recipients were tested for measurement of total chemical shrinkage; a) plastic tubes ($\phi = 25$ mm, $h = 75$ mm), glass tubes ($\phi = 25$ mm, $h = 150$ mm) and glass Erlenmeyer flasks (conical form with 50 ml volume).

The plastic tubes were tried out in order to avoid any reaction between the alkalies in the cement and the glass. However, the plastic tubes did not perform satisfactorily, since pressing the silicon rubber stopper into the tube resulted in a subsequent slow expansion of the tube interpreted as a shrinkage.

The glass tube was filled with about 1 cm height of cement paste, while the rest (about 45 ml) was filled with water, oil or air (see section 3.1.3). The reproducibility of glass tubes filled with water was good as shown in Figure 1.

The Erlenmeyer flasks were chosen for two reasons:

1) According to Geiker /5/ the diameter of the test tube affects the measurements of the total chemical shrinkage. A small diameter resulted in a stepwise shrinkage-time profile, starting at a degree of hydration $\alpha = 0.6$. This phenomenon was observed in particular in tubes with diameter 7 mm, and to a lesser extent in tubes with 17 mm diameter. The observed behaviour was explained by adhesion between paste and tube. In such a case the release of the stresses built up during hydration would result in a stepwise measured shrinkage.

2) Using recipients with a larger diameter has the advantage of increasing the surface-to-volume ratio of the paste. A higher mass of cement paste will lead to higher accuracy, as long as sufficient water permeability is maintained (see section 3.1.4). The surface of the contact zone at a height of 1 cm is about 5 times larger for the Erlenmeyer flask than for the glass tube, which will ease the imbibition of water.

In general, a 1 cm thick layer of paste (about 35 g) is placed in the Erlenmeyer flask, while the rest (about 45 ml) is filled with water or possibly oil (see section 3.1.3). The reproducibility of erlemeyer flasks filled up with water is very good (see Figure 1).

3.1.2 Effect of the stopper

Since the stoppers plugging the recipients were made out of rubber, the possibility exists that they may deform during the first hours, resulting in false measurements. In order to investigate this effect, three Erlenmeyer flasks were filled with water, the stoppers with pipette were placed, the water levels were followed the first 48 h and the corresponding volume changes

were plotted as shown in Figure 2. Note that the scale of the ordinate axis is enlarged due to the small magnitudes of volume changes. Furthermore, the major fraction of the stopper deformation seems to happen the first hour. Realizing that the precision of the technique is ± 0.005 ml, the effect of the stopper deformation can be neglected.

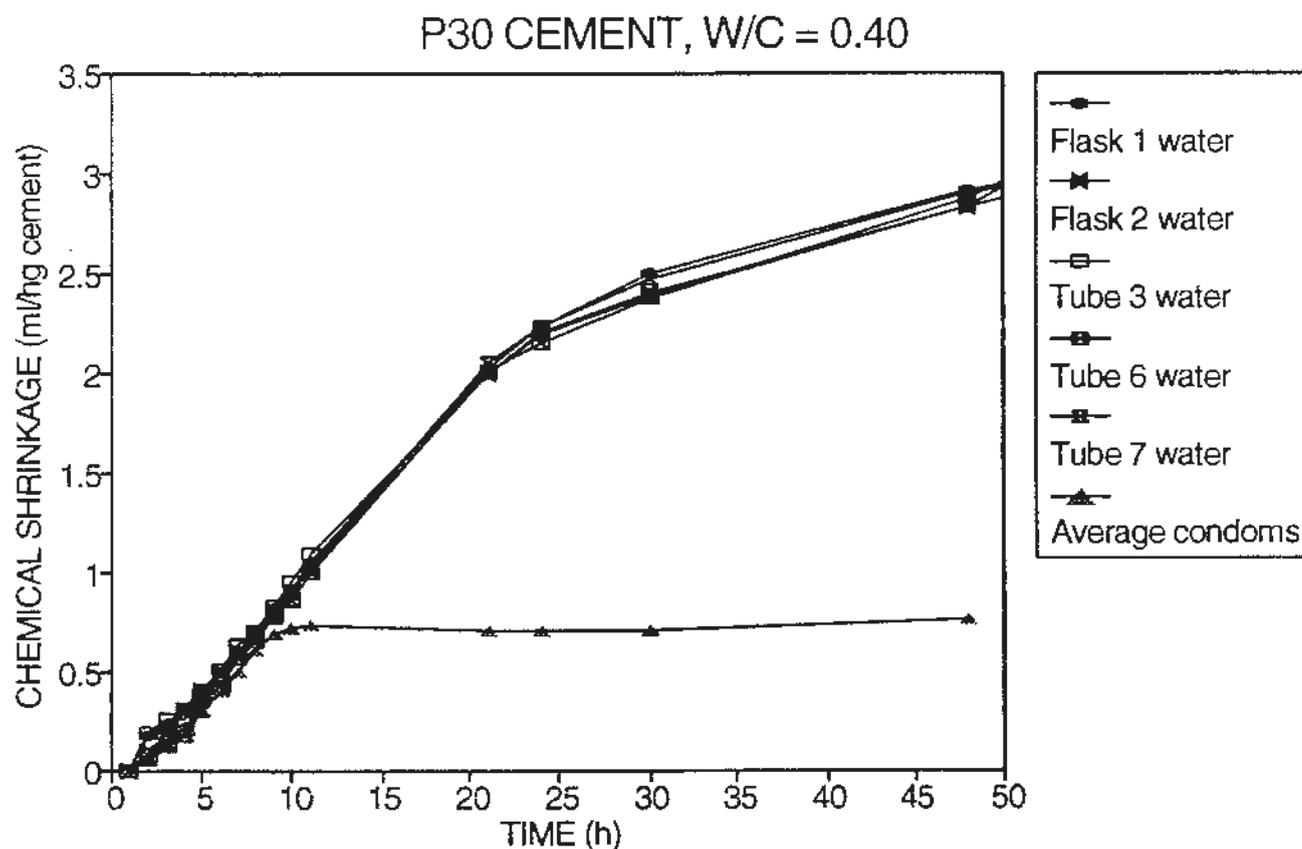


Fig. 1 Comparison of total chemical shrinkage of P30 cement with $w/c = 0.40$ measured with glass tubes and Erlenmeyer flasks filled up with water. The average external chemical shrinkage curve is included as well.

3.1.3 Effect of dissolution of salts from the cement

After the paste is put in the recipient, it is normally filled up with water. A possible source of error is thus the dissolution of ions from the cement into the water phase. The removal of salt from the paste would lead to a volume decrease greater than the subsequent slight expansion of the solution. Thus, a net volume decrease would be the result. The greater amount of excess water above the paste, the greater mass of sparingly soluble salts (e.g. calcium hydroxide and gypsum) will be dissolved and the lower the concentration of readily soluble salts (e.g. alkali salts) in the water phase will be. The former case (i.e. fixed concentration) could lead to increased shrinkage, while the latter case (i.e. diluted concentration) could affect the reaction rates. Therefore, it was tried to reduce the water volume by replacing some of it by air or oil:

If only a little water is added on top of the paste and the tip of the pipette is below the water level, the major part of the recipient is filled with air and the potential leaching problem should be minimized. However, the results seemed to be very dependent of the ambient temperature and handling. Holding the recipient by hand expanded the air due to the heat transfer, which increased the level in the pipette immediately. Thus, this experimental set up was abandoned.

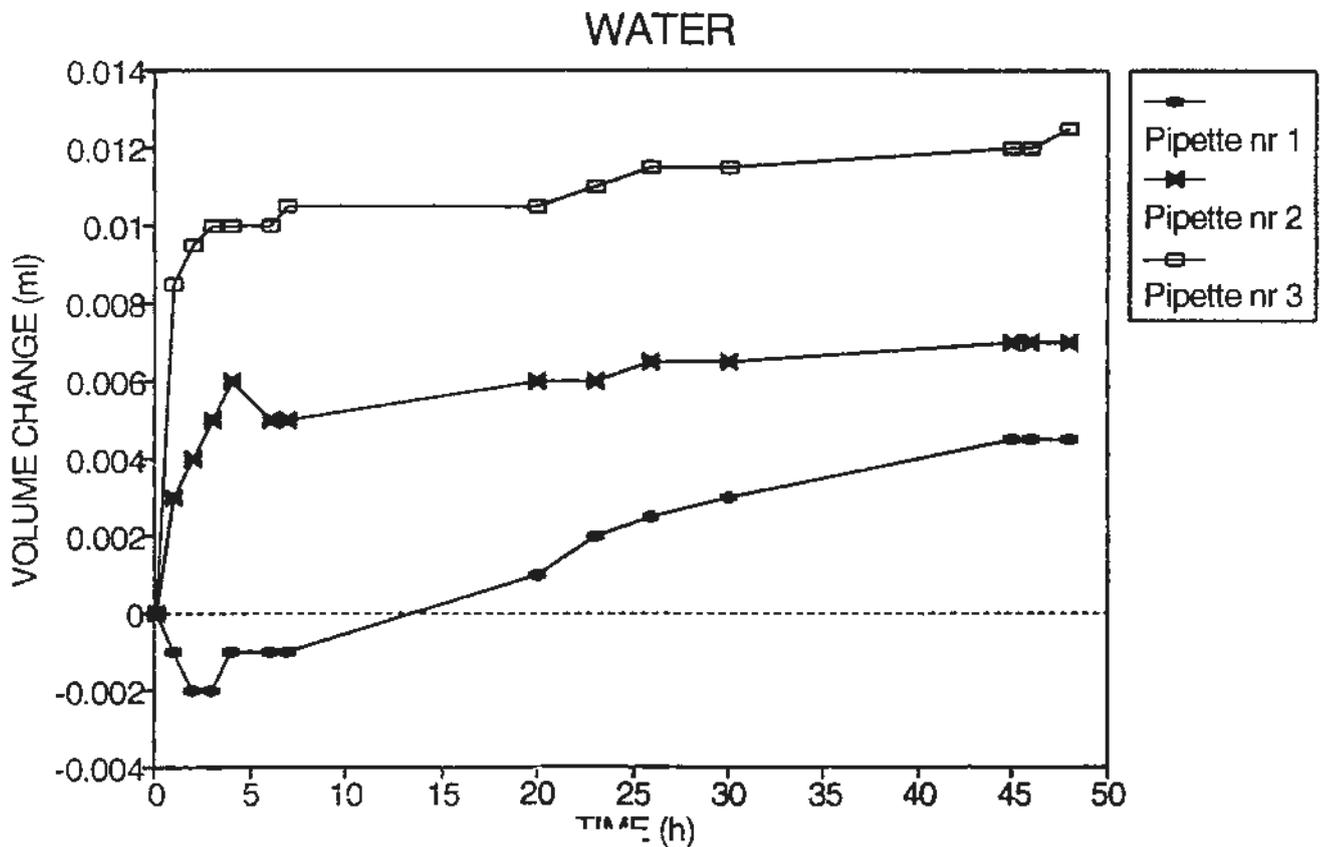


Fig. 2 Influence of the deformation of stoppers on the measurement of the total chemical shrinkage.

By adding only a few ml of water on top of the cement and filling the rest of the recipient with oil, the potential leaching problem should be avoided. However, the total chemical shrinkage seemed to be higher when using recipients filled with oil, as seen by comparing Figures 1 and 3. The reason is probably that the rubber stoppers absorbed oil and swelled, which resulted in a slow movement upwards being interpreted as increased shrinkage. The oil reduced the friction between glass and rubber, and some of the stoppers even popped out of the tubes. Furthermore, a white precipitate on the interphase between oil and water was observed, which may affect the measurements as well. In addition, the reproducibility of the water filled recipients are much better. In both cases, however, during the first hours the total and external chemical shrinkage are close to another as predicted and revealed if they are compared in Figures 1 and 3. Thus, recipients filled with water are recommended if the potential leaching problem may be neglected (see section 3.1.4).

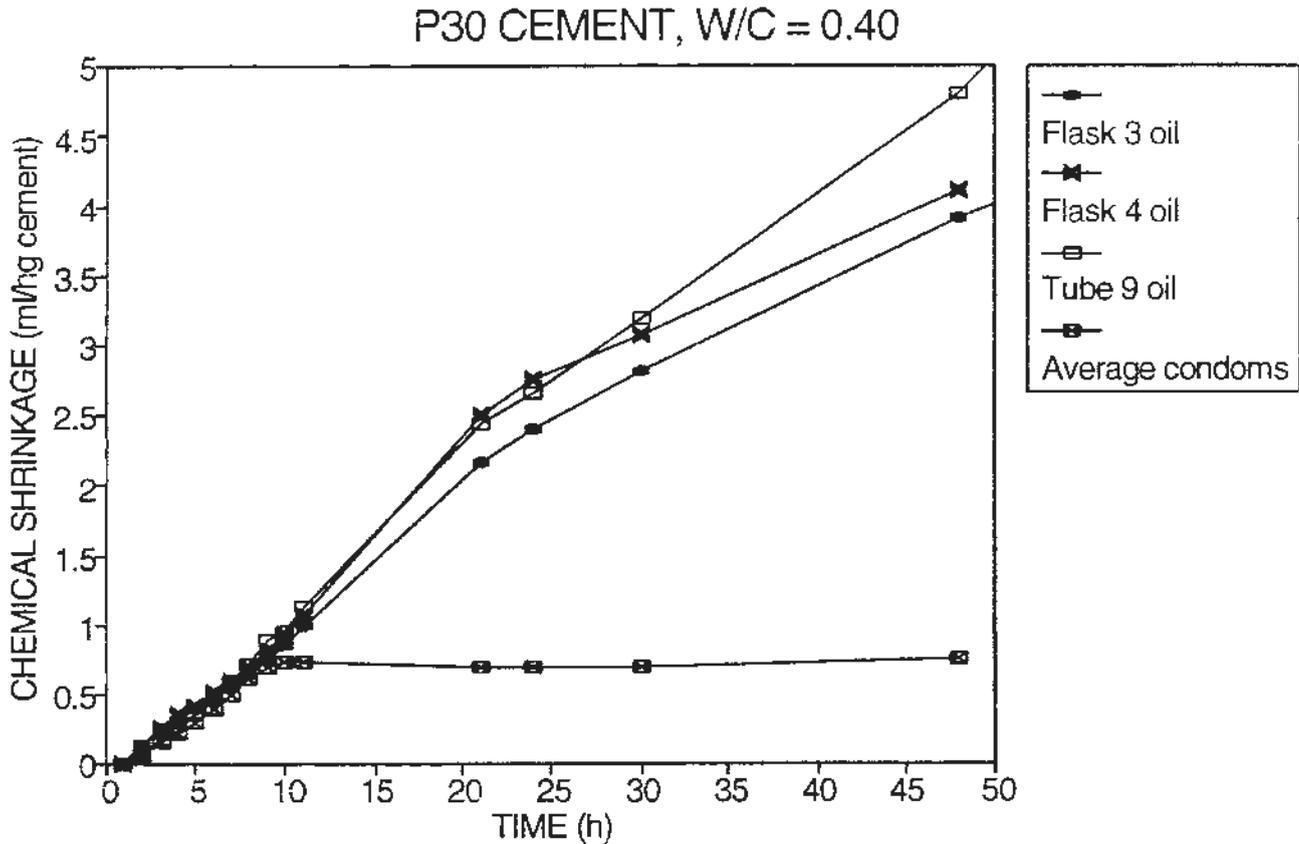


Fig. 3 Comparison of total chemical shrinkage of P30 cement with $w/c = 0.40$ measured with glass tubes and Erlenmeyer flasks filled up with oil. The average external chemical shrinkage curve is included as well.

3.1.4 Effect of paste thickness

According to Geiker /5/, increasing the sample thickness causes a decrease in measured total chemical shrinkage at later ages (> 150 h). This is because not all the contraction pores are filled with water due to decreased permeability and increased length of permeation path. The effect will occur earlier if the w/c is low or pozzolanic additives (e.g. silica fume) are included in the paste.

In order to investigate this effect during the first 48 h of interest in the present study, 6 erlenmeyer flasks were filled with cement paste from the same mix in thicknesses ranging from 3 mm to completely filling the flask. The total chemical shrinkages (ml/100 g cement) as a function of the logarithm of time (h) are plotted in Figure 4.

The plots in Figure 4 reveal that the paste thickness has an influence on the measurement of the total chemical shrinkage, corresponding to a maximum difference of 0.22 ml/100 g cement

after 9 hours and a tendency of greater shrinkage for thinner paste layers (and more excess water, see section 3.1.3). The reason for this may be that the water has difficulties in reaching the initial contraction pores in the center for the thicker paste layers, since the driving force of the under pressure still is low. After 9 hours the plots are converging. The difference after 24 hours becomes only 0.035 ml/100 g cement. This may be due to the contraction pores which at this time (much higher degree of hydration) has developed sufficient under pressure to suck the water through the hardening paste.

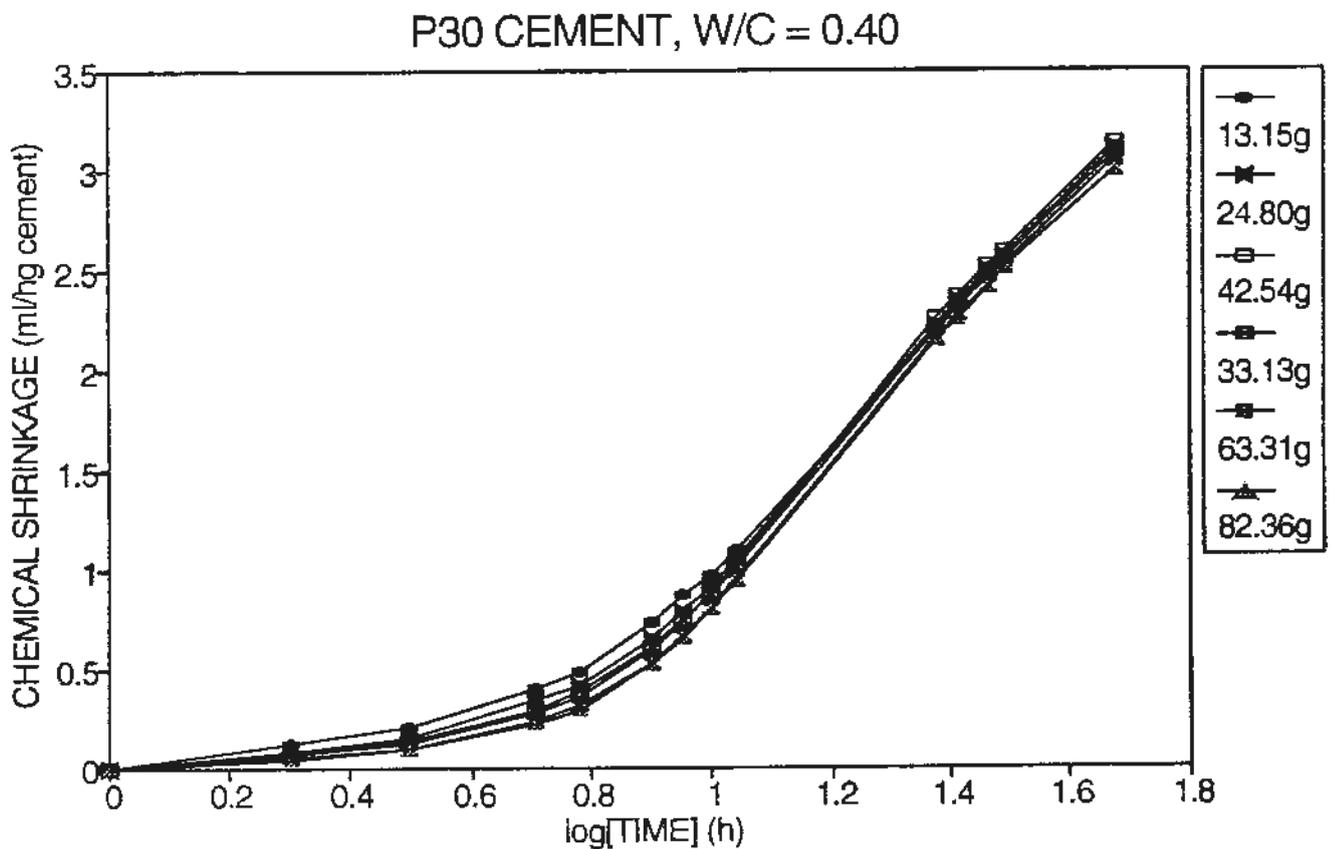


Fig. 4 Influence of the paste mass (i.e. indirectly thickness) on the measurement of the total chemical shrinkage the first 48 hours (logarithmic abscissa).

The observation in Figure 4 may also be caused by the decreasing amount of excess water with increasing thickness of cement paste layer. The dilution of readily soluble salts (see section 3.1.3) at lower paste loadings may accelerate the early hydration, while the rate of hydration rapidly becomes diffusion controlled by the precipitating CSH gel so the effect is canceled out after a while (> 16 h). A greater dissolution of sparingly soluble salts (see section 3.1.3) would only lead to a parallel displacement of the curves.

The mechanism of the first explanation is likely to dominate, but the contribution of the latter effect may be investigated by comparing two experiments; one flask with paste filled up with water and another filled up with for instance a 1 % potassium hydroxide solution.

3.2 External chemical shrinkage

3.2.1 Effect of a leak in the elastic membrane

It happens that the elastic membrane of the condom is punctured during an experiment, in particular when it is put in or removed from the weighing basket. A leak from the beginning may also occur if the silicon glue sealing is not placed properly. In order to investigate the consequences of this effect (i.e. to be able to spot a leak by the shape of the shrinkage-time profile), 5 samples were made out of one mix based on P30 cement and $w/c = 0.30$ (no bleeding mix, see section 3.2.5). The condoms of these samples were punctured with different hole sizes at different times; 1) no hole, 2) small hole after 4 h, 3) small hole after 7 h, 4) big hole after 25 h and 5) complete condom removal after 50 h, and the impact on the external chemical shrinkage-time profile is revealed in Figure 5.

When accidentally a condom breaks before the "flattening out level" (i.e. very low external chemical shrinkage rate) is reached (sample no. 2 in Fig. 5), nothing will happen at once since excess water still is available in the paste anyway. However, when the paste has formed a rigid skeleton the structure remains saturated since water is sucked in through the hole driven by the under pressure created by the contraction pores. Since the paste absorbs water, the density increases and the higher measured mass of the sample is erroneously interpreted as a volume decrease. The curve of the punctured sample (no. 2) only separates from the whole one (no. 1) when the latter starts flattening out. Sample no. 2 is actually behaving as a total chemical shrinkage sample as long as the paste is porous enough to ensure filling of the contraction pores.

When the condom is punctured immediately after the flattening out level is reached, as for sample no. 3 in Figure 5, a similar behaviour as for sample no. 2 is observed, but it flattens out on a lower level.

The rate and magnitude of the apparent volume decrease (i.e. mass increase) after a leak occur is determined by the size of the hole and the time of puncture. Comparing the shrinkage curve for the sample with a hole made after 25 h (no. 4) with the curve for the sample where the complete condom was removed after 50 h (no. 5) in Figure 5, the apparent shrinkage rate is larger for the latter. Thus, a bigger hole gives a higher rate. Comparing the shrinkage curves in Figure 5 for the samples no. 2, 3 and 4 with holes made after 4, 7 and 25 h, respectively, the secondary flattening out level is lower the later the puncture was made. This is due to the lower permeability of the paste at higher ages, and the later the puncture is made the lesser fraction of the contraction pores are filled (note that the diameter of the paste sample is around 50 mm).

In addition to observing a leak by the shape of the external chemical shrinkage-time curve, a visual control may easily be made as well if a transparent condom is used. Normally the paste turn grey when the flattening out level of the curve starts. In the case of a leak, the paste stays dark, especially around the spot of the puncture.

Although a leak will ruin the measurement of the external chemical shrinkage, it may easily be discovered as described in the preceding.

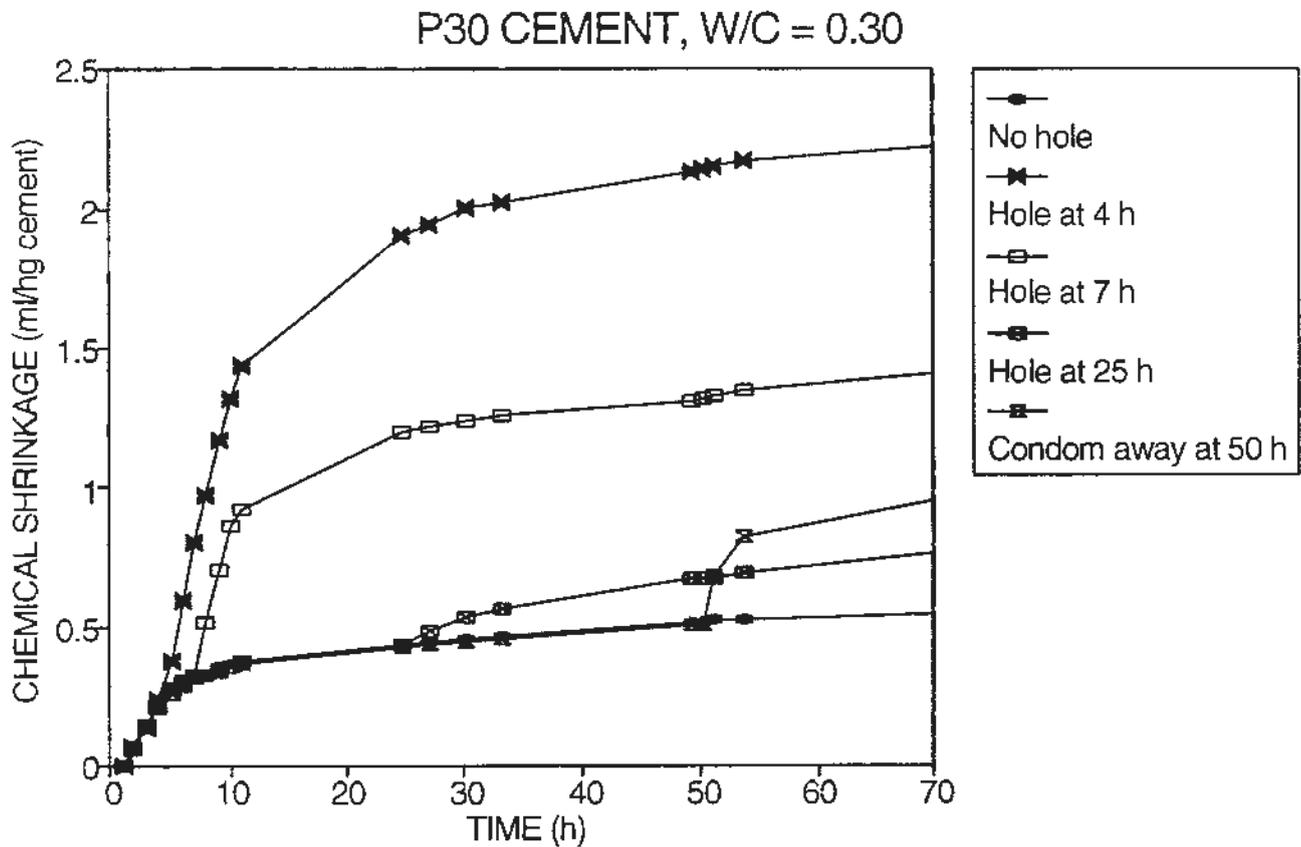


Fig. 5 Effect of the time of a leak in the condom on the external chemical shrinkage test.

3.2.2 Effect of enclosed air

The effect of air bubbles enclosed in the condom has been examined by enclosing different amounts of air in several samples of the same mix (P30 cement and $w/c = 0.40$). The consequence of the amount of enclosed air on the external chemical shrinkage-time profile is revealed in Figure 6. Air bubbles may either be entrained in the paste during mixing or trapped when the condom is not filled properly. Air in the condom may be avoided by vibrating the paste before it is placed into the condom, by filling it up carefully and by kneading and shaking the paste in the condom before closing it in order to let the bubbles rise.

The curves in Figure 6 reveal that enclosed air has no influence on the initial external chemical shrinkage, but has a significant impact on the value of the flattening out level. This may be explained by the vacuum of the contraction pores created after the hydration network is strong enough to resist the contracting forces. Firstly, the volume of the air is reduced proportionally to the amount of contracting pores formed as long as there is air voids enclosed. Secondly, the pressure of the air in the pores will be decreased from 1 atm. The behaviour is according to the ideal gas law. The first effect is leading to a higher apparent flattening out level with increasing air, as observed in Figure 6. The conclusion is that air in the condom has to be avoided when external chemical shrinkage is to be measured.

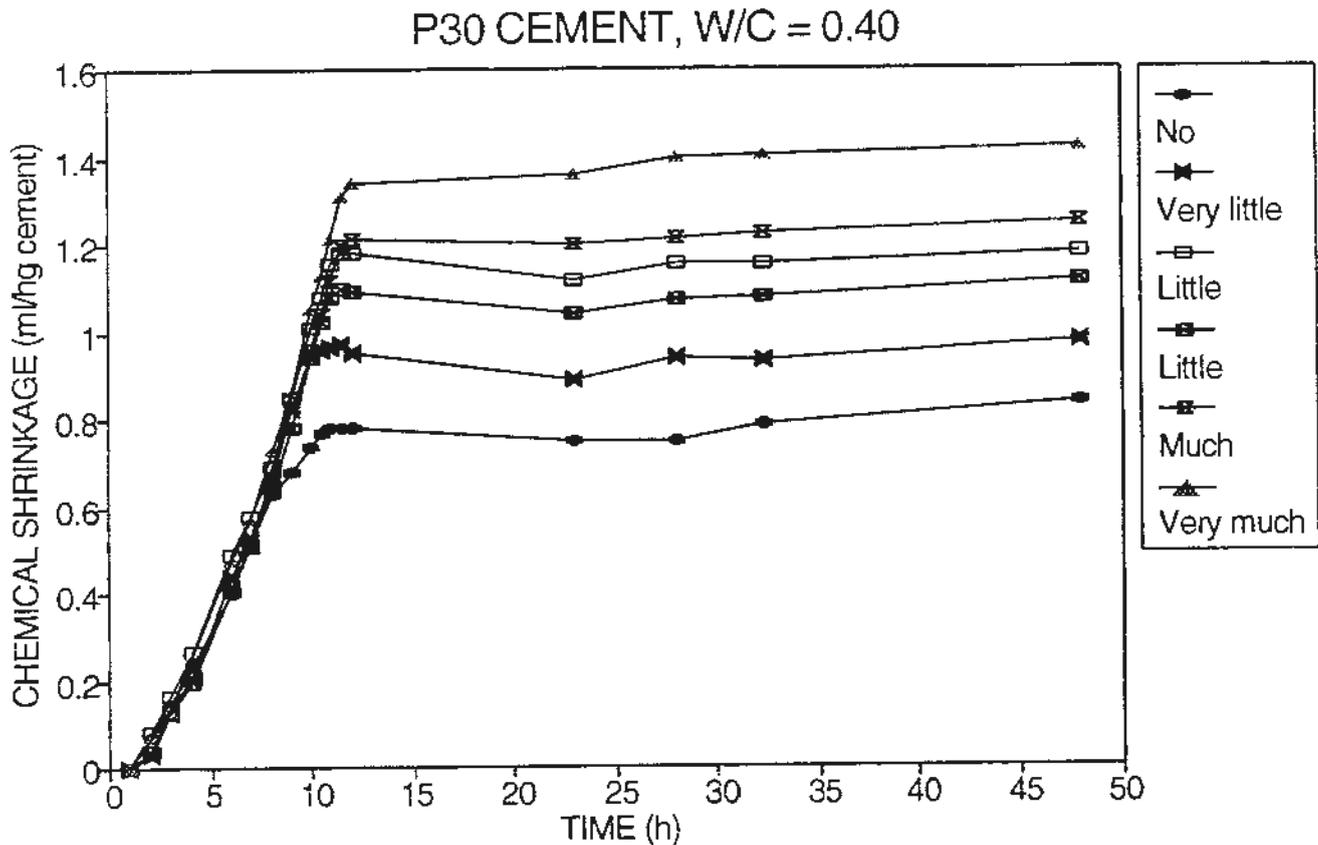


Fig. 6 The influence of amount of enclosed air in the sample on the external chemical shrinkage measurements.

3.2.3 Effect of the mass of the sample

In order to study the effect of the sample volume on the measurement of external chemical shrinkage, condoms were filled with different amounts of paste from the same mix (P30 cement and $w/c = 0.30$). The external chemical shrinkage-time curves are plotted in Figure 7.

The results presented in Figure 7 show that samples of mass lower than 250 g result in a too large relative error, which can be seen as an oscillation around the more stable curves. The explanation may be that the rubber is not stretched enough to follow the shrinkage as for the heavier samples. Samples of mass above 500 g are difficult to handle during weighing and the condom is stretched so much that it easily breaks. Sample no. 5 (520 g) and no. 6 (825 g) do not flatten out due to a rupture of the rubber (i.e. external water is sucked in as discussed in section 3.2.1). The conclusion is that the ideal weight of a filled condom is between 300 and 450 g.

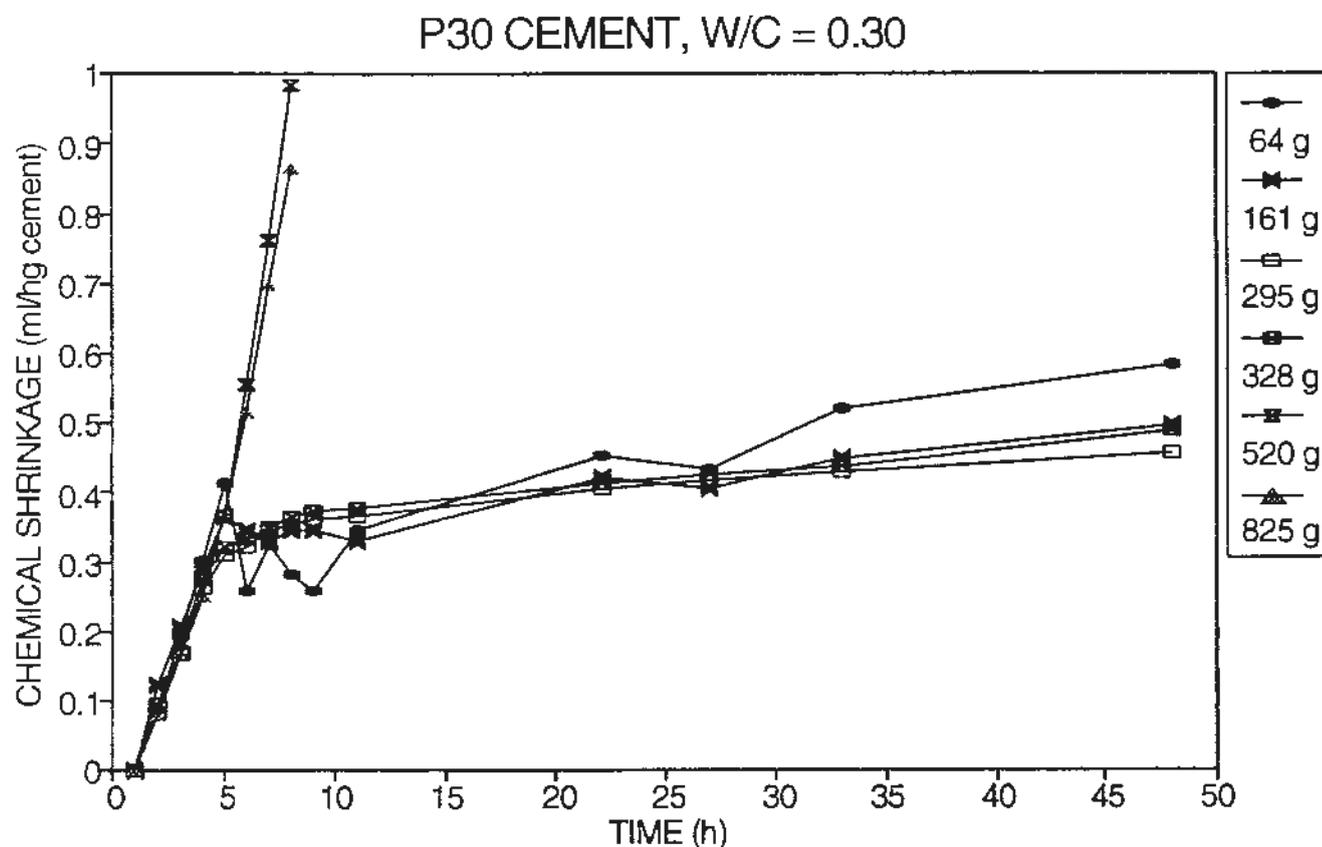


Fig. 7 The influence of the mass of the sample on the external chemical shrinkage.

3.2.4 Effect of the temperature in the sample

Since the sample mass in the external chemical shrinkage test (about 400 g) is much higher than in the total chemical shrinkage test (about 35 g), the temperature in the two different tests might differ, which will have an effect on the measured shrinkage. Three parallels for both external and total chemical shrinkage test were made, and the initial temperature was measured to 26.6 ± 0.2 °C for each of them 10 min after blending ingredients (P30 cement and $w/c = 0.40$) kept at 20°C. The temperature in the samples were logged as a function of time, and it turned out that the paste was in thermal equilibrium with the water bath at 20°C within 1 h. Since the first measurement in practice is done at the age of 1 hour, there is no influence of the initial temperature and its rate of declining to ambient temperature.

However, there was a difference of +1°C in the second heat peak (i.e. corresponding to maximum hydration rate) between the samples of the external and total chemical shrinkage, respectively. This temperature difference results in a measured shrinkage difference of about 0.01 ml/100 g cement due to the change in water density with temperature. This slight temperature difference may, together with the difference in salt concentrations (see section 3.1.3), explain why the initial external shrinkage not always is exactly the same as the total chemical shrinkage for the same mix (usually only minor differences are observed).

3.2.5 Effect of bleeding of the cement paste

Bleeding occurs when the suspension of cement particles becomes unstable under the forces of gravity. This happens before and during the dormant period and the rate of separation is dependent on the fineness of a cement (finer cement \rightarrow slower separation) and the w/c ratio of a cement paste (higher w/c \rightarrow faster separation). However, these tendencies may not always be valid when different cements are compared in series (e.g. decreasing fineness), due to differences in mineralogy of the cements.

Two series were made in order to study the effect of bleeding; P30 cement pastes with w/c ranging from 0.30 to 0.50 and P30 cement with w/c = 0.50 and 5, 10 and 15 % additions of fine, presumably inert filler (precipitated CaCO_3 with $S = 18 \text{ m}^2/\text{g}$ according to BET). The latter series was made in an attempt to avoid the bleeding effect. The external chemical shrinkage-time profiles of the w/c series are plotted in Figure 8, while the analogous data for the filler series are presented in Figure 9.

The bleeding water, and the imbibition of it, can easily be seen due to the transparency of the condom. It may also be observed that the colour of the specimen turns from dark to light grey when the contact surface between the rubber and its content becomes dry; the flattening out level starts. That is, after the skeleton of interconnecting hydration products is strong enough to resist the contracting forces created by the chemical shrinkage, the under pressure set up by the contraction pores will suck the bleeding water into the paste and the volume decrease (directly proportional to the volume of contraction pores) will erroneously be interpreted as external chemical shrinkage. A secondary, false flattening out level will be registered when the imbibition of the bleeding water is complete.

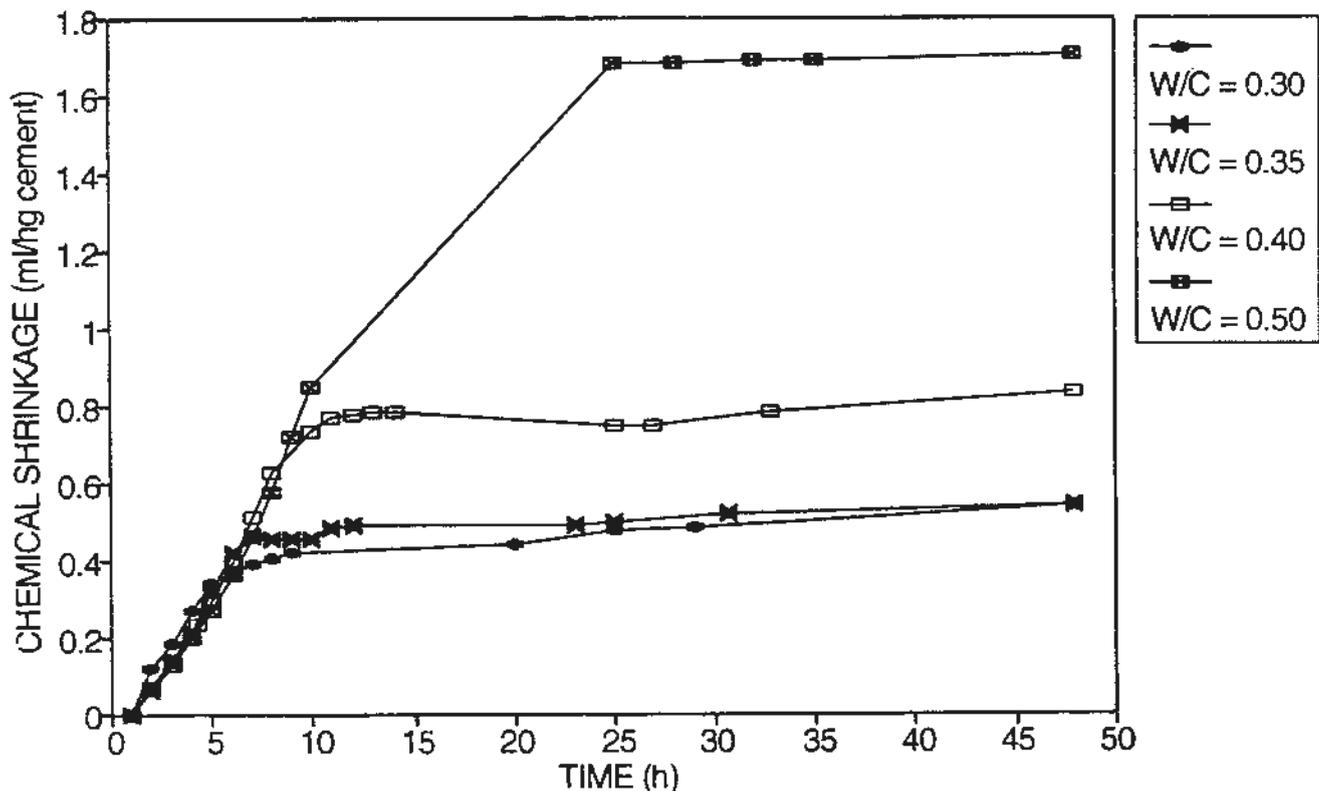


Fig. 8 The apparent external chemical shrinkage of P30 cement paste with different w/c.

The much higher flattening out level observed for the P30 cement paste with $w/c = 0.50$ compared to the lower water-to-cement ratios in Figure 8 is probably due to extensive bleeding. The cement grains in the slurry will segregate until there is contact between the particles or their initial hydration products (e.g. ettringite). The segregation of the $w/c = 0.35$ paste is probably negligible compared to the paste with $w/c = 0.30$ for such a fine cement as P30. Another effect that may add to the bleeding effect, is that the initial setting time (i.e. the start of hydration network formation) will increase with increasing w/c . The latter effect can be seen by comparing the early shrinkage curves in Figure 8. However, note that the final flattening out levels for P30 cement pastes with $w/c = 0.30$ and 0.35 are about equal, indicating that the bleeding effect is negligible and suggesting that a similar degree of hydration in the two pastes is necessary to form a rigid hydration network that can resist the under pressure set up by the contraction pores for both pastes.

A secondary effect of the sedimentation is that the effective w/c of the paste will be lower than the nominal w/c . This means that a rigid skeleton of hydration network may be built earlier since the particles initially are brought closer. The flattening out level might be slightly lower for this reason, counteracting the bleeding effect.

Figure 9 shows that the flattening out level for the external chemical shrinkage of a P30 cement paste with $w/c = 0.50$ is decreased substantially with increasing dosages of a fine calcite filler. The main reason is reduced bleeding. However, this filler is so fine ($18 \text{ m}^2/\text{g} \rightarrow$ particle diameter of about $0.1 \mu\text{m}$) that it will decrease the particle-particle distance.

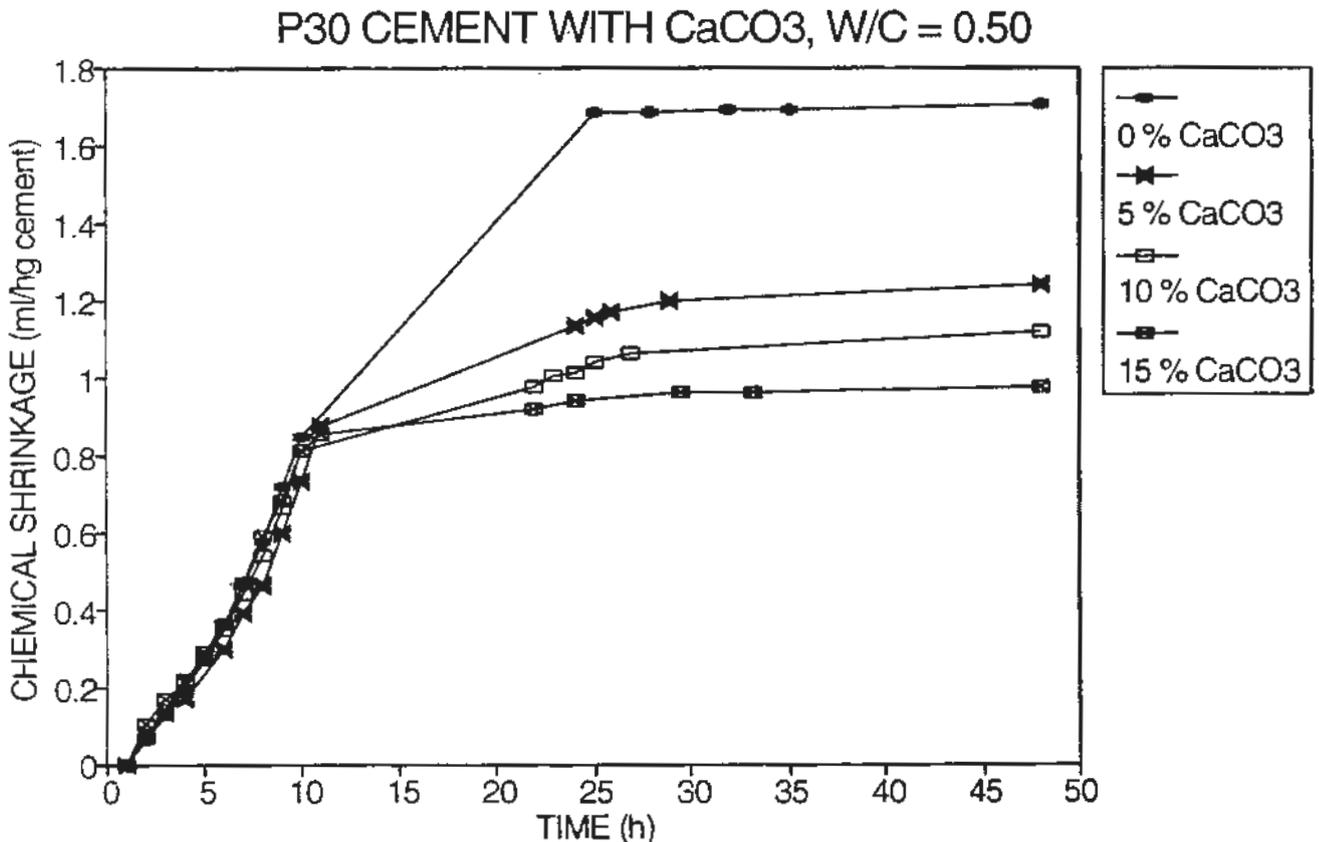


Fig. 9 The external chemical shrinkage of P30 cement paste with $w/c = 0.50$ and different additions of a fine calcite filler.

In addition, calcite filler additions may accelerate the early hydration rate. Thus it may cause a faster bridging of the cement grains when the hydration starts and for that reason (i.e. a more rigid skeleton at a lower α) lead to a lower flattening out level. The different factors are difficult to separate, and the method is not recommended to avoid the bleeding effect.

Setter and Roy /6/ tried to overcome the problem of bleeding by removing the bleeding water from one specimen and comparing the results with a specimen where the bleeding was not removed. However, the comparison is problematic since the effective w/c is changed.

Buil and Baron /7/ used a very low water-to-cement ratio (w/c = 0.27) to avoid bleeding. However, the results of mixes with only such a low w/c are of limited practical interest alone.

For practical studies (i.e. relating shrinkage of paste to concrete deformation), a filler corresponding to the fine fraction of the concrete might be used. In this way, bleeding might be minimized and the results have some practical meaning.

For fundamental studies of pure cement pastes, the only way to avoid bleeding and maintain a medium to high w/c is to rotate the sample under water. This approach is followed in the current and future research by the authors.

4. CONCLUSIONS

The conclusions drawn from an evaluation of the dilatometry technique for total chemical shrinkage measurement based on 1) putting the paste in a recipient, 2) filling the rest of the recipient with water, 3) plugging the recipient with a stopper with a water filled pipette stuck through and 4) following the total volume change by reading the fall of the water level in the pipette versus time, are:

- * Erlenmeyer flasks are recommended as recipients to the usual tubes, since recipients with a larger diameter has the advantage of increasing the surface-to-volume ratio of the paste. A higher mass of cement paste will also lead to higher accuracy.
- * The paste thickness and the excess water phase do not seem to affect the measurement of total chemical shrinkage the first 48 h, with the exception of a minor difference in the period 3-12 h.

The conclusions drawn from an evaluation of the method for measurement of external chemical shrinkage based on Archimedes principle (the external shrinkage of cement paste filled in an elastic rubber bag (i.e. condom) will lead to a reduction in buoyancy, which will be directly measured as a weight increase under water) are:

- * The optimum mass of the sample enclosed in an ordinary condom as elastic bag, is between 300 and 450 g.

- * Erroneous measurements due to a leak in the membrane is easy to discover both due to the shape of the external chemical shrinkage-time curve and by the colour of the sample seen through the transparent elastical membrane.
- * Measures must be taken to avoid entrained air in the mix or entrapped air in the condom, as that will lead to the recording of an erroneously high external chemical shrinkage.
- * The true external chemical shrinkage can only be measured for stable cement pastes, since bleeding will lead to erroneously high values. If no stabilizing additives or admixtures are added, the true external chemical shrinkage of cement paste with w/c ranging from 0.35 upwards can only be measured by continuous rotation of the sample interrupted by the weighing.

Acknowledgement. The study results from the student exchange program ERASMUS between "Katholieke Universiteit van Leuven" and "Norges Tekniske Høgskole i Trondheim". We would like to thank Prof. D. van Gemert, Belgium, for making this exchange possible.

5. REFERENCES

- /1/ Powers, T.C.: "Structure and Physical Properties of Hardened Portland Cement Paste", J. Am. Ceramic. Soc., Vol. 41, No. 1, 1958, pp 1-6.
- /2/ Knudsen, T. & Geiker, M.: "Chemical Shrinkage as an Indicator of the Stage of Hardening", Proceedings of the International RILEM Conference on Concrete of Early Ages, Vol. I, Session V: "Methods of Indicating the Stage of Hardening", Ecole National des Pouts et Chaussees, Paris, April 6-8, 1982, pp 163-167.
- /3/ Jensen, O.M.: "Autogen Deformation og RF-ændring - selvudtørring og selvudtørringsvind", Dr. Thesis TR 284/93 (ISSN 0907-7073), The Technical University of Denmark, Department of Civil Engineering, Building Materials Laboratory, May 1993, 117 pp (in Danish).
- /4/ Paulini, P.: "Reaction Mechanisms of Concrete Admixtures", Cement and Concrete Research, Vol. 20, 1990, pp. 910-918.
- /5/ Geiker, M.: "Studies of Portland Cement Hydration. Measurements of Chemical Shrinkage and a Systematic Evaluation of Hydration Curves by means of the Dispersion Model", Dr. Thesis, Institute of Mineral Industry, Technical University of Denmark, 1983.
- /6/ Setter N. and Roy, D.M.: "Mechanical Features of Chemical Shrinkage of Cement Paste", Cement and Concrete Research, 1978, Vol. 8, pp. 623-624.
- /7/ Buil, M. and Baron. J.: "Le retrait autogène de la pâte de ciment durcissant", 7th International Conference on the Chemistry of Cement, 1980, Volume VI, pp 37-41 (in French).