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Chemical shrinkage of oil well cement slurries

H. Justnes,[*] D. van Loo,[†] B. Reyniers,[†] P. Skalle,[‡] J. Sveen[‡] and E. J. Sellevold[§]

SINTEF STRUCTURES AND CONCRETE: KUL; NTH

The phenomenon of 'gas migration' in oil well cementing is believed to occur during the transition state between initial and final set of the cement. As part of an initial study to elucidate the mechanism of gas intrusion into the cementing material, the external and total chemical shrinkage of API class G cement slurries was measured for the first 48 h of curing. In order to counter the disturbance of segregation and formation of bleed water during the measurement of external chemical shrinkage, precipitated calcium carbonate ($\leq 15\%$, fineness 18 m^2/g) and the viscosifier polyvinylalcohol were added. Neither addition significantly influenced the hydration rate of G cement with water–cement ratio (w/c) = 0·50 during the first 48 h. The chemical shrinkage, both total and external, of G cement slurries on hardening seems to be largely independent of w/c in the first 48 h. The external and total shrinkages of a neat G cement slurry curing at 20°C and atmospheric pressure are about 1·0 ml/100 g cement or 1·2 vol.% and 2·2 ml/100 g cement or 2·6 vol.% respectively after 48 h.

Introduction

Gas leakage in the annulus after primary cementing of oil and gas wells is still a problem, in particular in upper, unconsolidated, cavernous holes and in deep wells, i.e. under high temperature and high pressure (HTHP) conditions. Reasons for and mechanisms of gas migration are presented elsewhere.[1–3] Annular gas flow may occur when

(*a*) the hydrostatic pressure falls below the formation pore pressure due to shrinkage, fluid loss or gel strength build-up

(*b*) if the cement slurry stays permeable or the initial gas forms channels, micro-annuli or fractures before the slurry has reached a certain strength.

Thus, the phenomenon of gas migration is believed to occur during the transition state between initial and final set of the cement when the pressure transferred by the cement slurry column changes from being given by the density (i.e. $P = \rho g h$, where P is pressure, ρ is density, g is the gravitational constant and h is height) of the cement slurry to the density of the percolating water phase, or is even lower.

As part of an initial study to elucidate the mechanism of gas intrusion into the cementing material, the external and total chemical shrinkages of API class G cement slurries were measured during the first 48 h of curing. While the external chemical shrinkage expresses the volume change of the slurry leading to a possible micro-annulus between the slurry and the casing, the total chemical shrinkage is the sum of external chemical shrinkage and the volume of empty contraction pores of the slurry at all stages. The formation of empty contraction pores dominates when the built-up network between the particles in the matrix becomes strong enough to resist the forces created by the total shrinkage (i.e. the difference in volume between reactants and products). Contraction pores contribute to the continuity of the porosity in a set cement slurry, which influences the permeability.

The present investigation is the second in a series of three to elucidate fundamental aspects of the phenomenon of gas migration during oil well cementing: porosity,[4] chemical shrinkage and dissolved gas.[5]

Experimental details

Components

The Norwell G cement (American Petroleum Institute

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[*] SINTEF Structures and Concrete, N-7034 Trondheim, Norway.

[†] KUL, Department Burgerlijke Bouwkunde, B-3001 Heverlee, Belgium.

[‡] NTH, Department of Petroleum Engineering and Applied Geophysics, N-7034 Trondheim.

[§] NTH, Department of Structural Engineering, N-7034 Trondheim.

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classification) was delivered by Norcem, Brevik, Norway, and had the following analysis: 64·82% CaO, 22·00% SiO_2, 4·78% Fe_2O_3, 3·53% Al_2O_3, 1·75% SO_3, 1·42% MgO, 0·87% free lime, 0·60% alkalis and 0·37% loss on ignition. The Blaine specific surface was 300 m^2/kg. The water was distilled before use. Precipitated calcium carbonate was used as a filler additive and polyvinylalcohol (PVA) was used as a viscosifying admixture, both in order to prevent separation ('bleed') of the cement slurry. The calcium carbonate was of the quality 'Puriss Ph Eur (>99%)' from E. Merck, Darmstadt, Germany. The specific surface of the calcium carbonate was determined by nitrogen adsorption (BET) to 18 m^2/g. The PVA from E. Merck had a mean molecular weight of 72 000.

All the components for the cement slurry were kept at room temperature (20 ± 1°C). Norwell G cement (±1 g), water (±0·01 g) and additives or admixtures (±0·001 g) were weighed to make the slurry. The dry additives were mixed with the dry cement. The water was added at once and this moment was taken as the zero point on the time scale. The slurry was mixed for 2 min at 1000 rev/min and for 1 min at 1500 rev/min in a Hobart mixer. The bowl with the slurry was put on a vibration table in order to remove some of the entrained air. However, lengthy vibration was avoided to prevent bleed. Slurry used for the total and the external chemical shrinkage test was taken from the same mix.

Total chemical shrinkage

Cement slurry was put into three 50 ml Erlenmeyer flasks, forming a 1 cm thick layer in each. The mass of sample was determined by differential weighing. The remaining empty volume was then filled with distilled water, avoiding turbulence. A silicon rubber stopper was put in each flask, and a pipette was filled with water and inserted 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 flasks were put in a water bath at 20 ± 1°C. The position of the meniscus in the pipette was read hourly for 48 h. The decrease of the water column in ml gave the total chemical shrinkage directly (a drop of liquid paraffin on top prevented evaporation), which was expressed as ml/100 g cement (mean value from three parallels). The method relies on the assumption that all contraction pores are filled with water, which probably is correct at this early age and with such a thin sheet of cement slurry. The method is described and discussed in detail elsewhere.[6]

External chemical shrinkage

Three elastic rubber bags (i.e. condoms) were filled with cement slurry. Each condom was closed by twisting the upper part and tying it with a thin copper wire, and sealed by spraying silicone glue into the open end. The excess end part was cut off and the total mass determined.

The filled and sealed condoms were kept in a water bath at 20 ± 1°C. During the first 10 h, the condom was weighed every hour under water. From the Archimedes principle, an external shrinkage will lead to a reduction in buoyancy, which will be registered as a weight increase. Each condom was weighed in a basket under water, hanging on a scale. Between each pair of weighings, the sample was replaced carefully in the water bath as it was before in order not to disturb the skeleton and/or the bleed effect. The method is described and discussed in detail elsewhere.[6]

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

Results and discussion

The total chemical shrinkage of slurries based on G cement with w/c = 0·30, 0·40 and 0·50 as a function of time is shown from 1 to 48 h in Fig. 1. The external shrinkage profiles for the same mixes and period are shown in Fig. 2.

In theory, the *total* chemical shrinkage of a slurry <48 h old should be *independent* of the w/c, since the initial hydrate network is permeable enough to ensure free flow of water to the unreacted cement particles. Only more mature specimens may have a reduced hydration, and thereby shrinkage, with decreasing w/c due to a denser structure that, beyond a given stage, will control the hydration process by diffusion. Taplin[7] investigated the chemically bound water as a function of w/c and age for a cement paste and reported that the w/c should be less than 0·30 in order to measure any decrease in chemically bound water at 48 h. Accordingly, Fig. 1 demonstrates that the *total* chemical shrinkage curves are *identical* for the slurries with w/c = 0·30, 0·40 and 0·50.

From Powers'[8] rule of thumb that a cement binds 25% of its weight in water chemically during the hydration process, and that the total chemical shrinkage is about 25% of the chemically bound water, 100% hydration will lead to a total chemical shrinkage of 25 × 25/100 g cement = 6·25 ml/100 g cement. At 48 h the total chemical shrinkage of the G cement is 2·17 ml/100 g cement (see Fig. 1), which corresponds to a degree of hydration $\alpha = 2{\cdot}17/6{\cdot}25 = 0{\cdot}35$. The amount of total chemical shrinkage for the G cement at 48 h was confirmed by an independent investigation.[9]

The external chemical shrinkage, on the other hand, is apparently *not* independent of the w/c, as revealed in Fig. 2. The general profile of an external shrinkage curve is that it follows the total chemical shrinkage curve (as seen by comparing Figs 1 and 2) until the hydrate network has formed a strong enough skeleton to resist the contracting forces. At this stage (6–12 h) the external chemical shrinkage *rate* slows down drastically and the shrinkage — time curve flattens out. The flattening-out

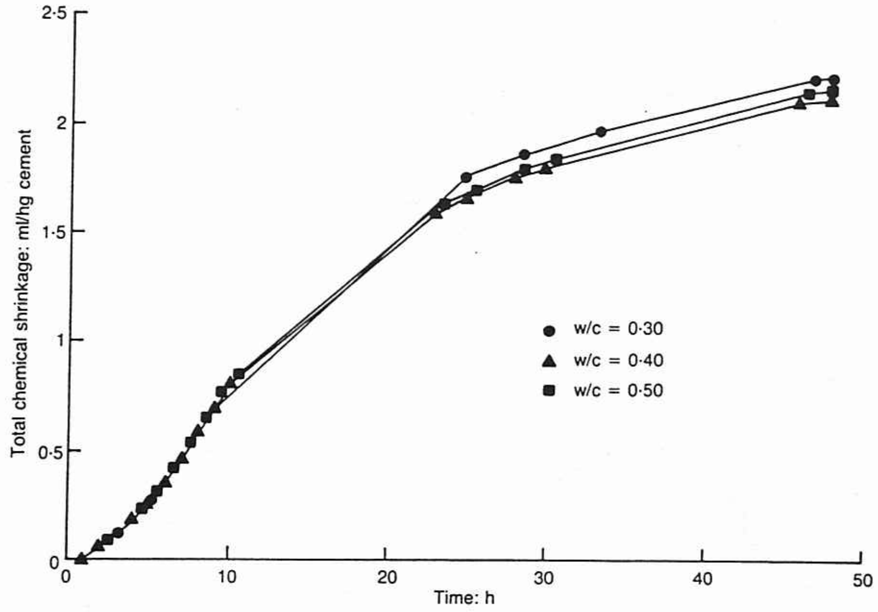

Fig. 1. The total chemical shrinkage of G cement slurries with various w/c values at 1–48 h age

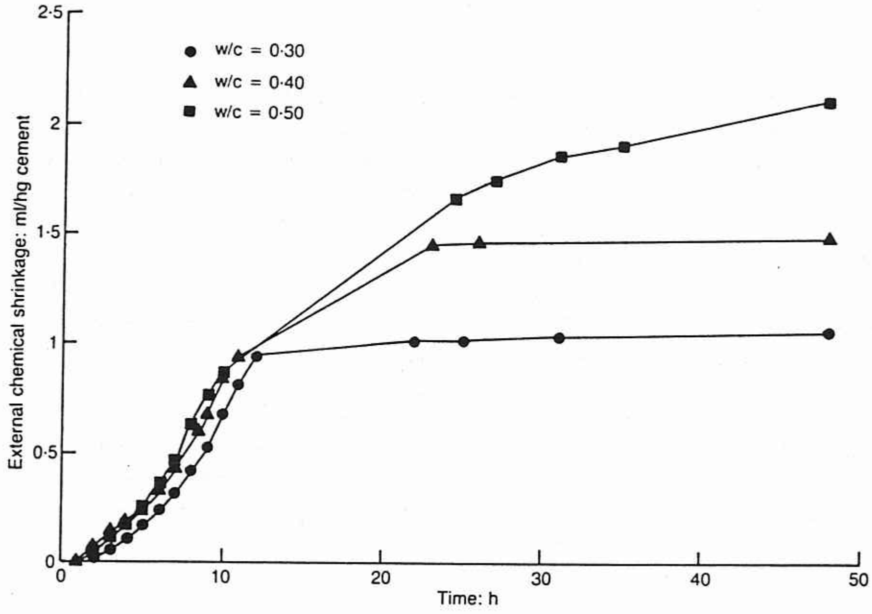

Fig. 2. The external chemical shrinkage of G cement slurries with various w/c values at 1–48 h age

level seems to decrease with decreasing w/c, being 1·05, 1·47 and 2·2 for w/c = 0·30, 0·40 and 0·50 respectively.

However, the possibility of separation of the cement slurry (bleed) may disturb the experimental results for the *external* chemical shrinkage. Norwell G cement is a rather coarse cement (300 m^2/kg), and w/c = 0·50 will create significant bleed (i.e. separated water due to slurry segregation). Only the mix with w/c = 0·30 probably had no bleed water. If the slurry has separated, the bleed water on top of the more closely packed slurry will be sucked into the matrix *after* setting due to the underpressure created by the empty contraction pores. This will be interpreted erroneously as external chemical shrinkage, being in reality the total chemical shrinkage of a slurry with reduced w/c.

A G cement slurry with w/c = 0·50 had added to it 10% and 15% precipitated $CaCO_3$ (18 m^2/g) in order to minimize or prevent the formation of bleed water. The external chemical shrinkage was measured for these two mixes, and is compared with the external shrinkage profile from 1 to 48 h for a slurry without $CaCO_3$ addition in Fig. 3. The identical external chemical shrinkage profiles for the first 7 h indicate that the calcium carbonate does not influence the early degree of hydration: pure calcium carbonate was expected to be chemically inert in a cement

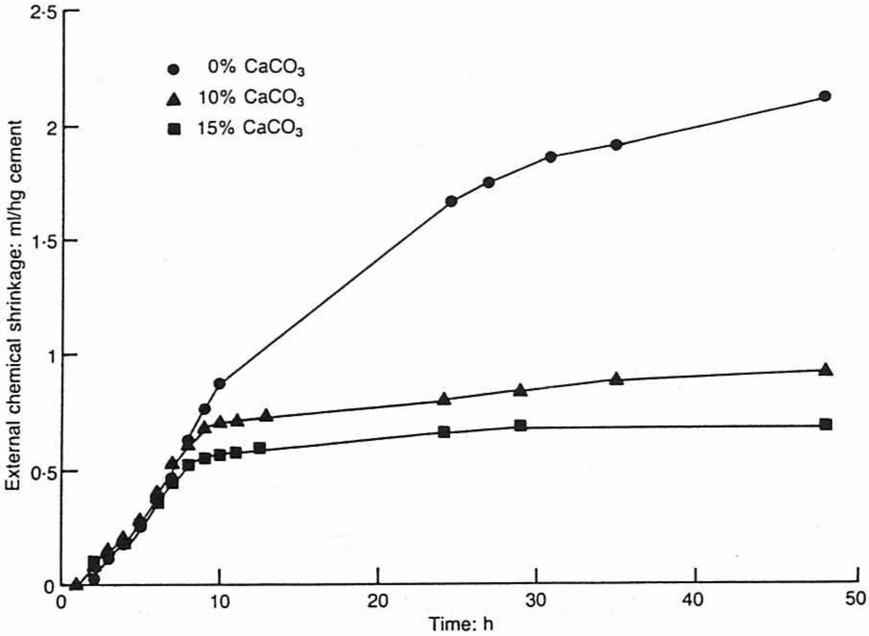

Fig. 3. The external chemical shrinkage of G cement slurries with w/c = 0·50 and various and precipitated calcium carbonate additions at 1–48 h age

slurry. The high specific surface of the calcium carbonate corresponds to an average spherical particle diameter of $d = 6/\rho \times S = 1 \cdot 2 \times 10^{-5}$ cm $= 0 \cdot 12$ μm, where ρ is the material density (g/cm^3) and S is the specific surface (cm^2/g). This is about the same size as condensed silica fume (usual specific surface 22 m^2/g), and the calcium carbonate particles will be distributed in the voids between close-packed cement grains (average diameter 40 μm). A closest packing of spheres with diameter d_1 = 40 μm would have given interstitial porosity with initial space for a smaller sphere with diameter $d_2 = (\sqrt{3/2} - 1)d_1 = 9$ μm in the cavity formed between four of the larger spheres lying in the corners of a tetrahedron and with contact along the edge of it. Fig. 3 reveals that there is a marked decrease in the flattening-out level from 0 (2·2 ml/100 g cement) to 10% (0·8 ml/100 g cement) calcium carbonate addition, while the change from 10% to 15% (0·6 ml/100 g cement) $CaCO_3$ is only moderate. The main effect is due to reduced bleed, while a minor effect may be caused by the packing of calcium carbonate particles between the cement grains, which establishes a rigid hydrate skeleton earlier, and would lead to a lower flattening-out level.

Another approach to counteracting the formation of bleed water is to add a viscosifier such as PVA. PVA is often used in the composition of oil well cement slurries in order to prevent loss of slurry fluid into the formation.[10] The total chemical shrinkage of G cement slurries with w/c = 0·50 and 0, 1%, 2% and 3% PVA of the cement weight is shown in Fig. 4 for 1–48 h. The *total* chemical shrinkage was measured in order to monitor whether or not the organic additive would retard the hydration reaction. The nearly identical total chemical shrinkage profiles in Fig. 4 reveal that the changes in the degree of hydration are insignificant. The external chemical shrinkage profiles for the same mixes and period are shown in Fig. 5. The flattening-out levels (external chemical shrinkage at 48 h) are about 2·2, 2·0, 1·7 and 1·1 ml/100 g cement for additions of 0, 1%, 2% and 3% PVA respectively. The decrease in flattening-out level is probably due to a decrease in amount of bleed water, since the viscosity of the slurry increased with increasing PVA addition. However, even the mixture with 3% PVA appeared to have a minor amount of bleed water, which was visible through the transparent condom.

Comparing the flattening-out level for the external chemical shrinkage of G cement slurry with w/c = 0·30 (1·05 g/100 g cement from Fig. 2), with w/c = 0·50 and 10% $CaCO_3$ (0·8 ml/100 g cement from Fig. 3) and with w/c = 0·50 and 3% PVA (1·1 ml/100 g cement from Fig. 5), and considering the above discussion, it is reasonable to state that the true external shrinkage at atmospheric pressure, corrected for bleed water, of G cement slurries is about 1 ml/100 g cement or 1·2 vol.% at 20°C, and is largely independent of w/c.

The independence of the flattening-out level of external chemical shrinkage for a cement slurry with respect to w/c has recently been confirmed[9] by slow rotation of the condoms in order to prevent separation, which implies that the calcite filler is better than PVA (slow bleed) at the present dosages in counteracting the formation of bleed water.

Chenevert and Shrestha[11] found an external chemical shrinkage of 4%–3% for different cement slurries cured at 100–435°F (38–225°C) and 1200–17 600 lb/in^2 (8·28–121·4 MPa). Increasing pressure may increase the flattening-out level of external chemical shrinkage, since the differential pressure between the pores and the

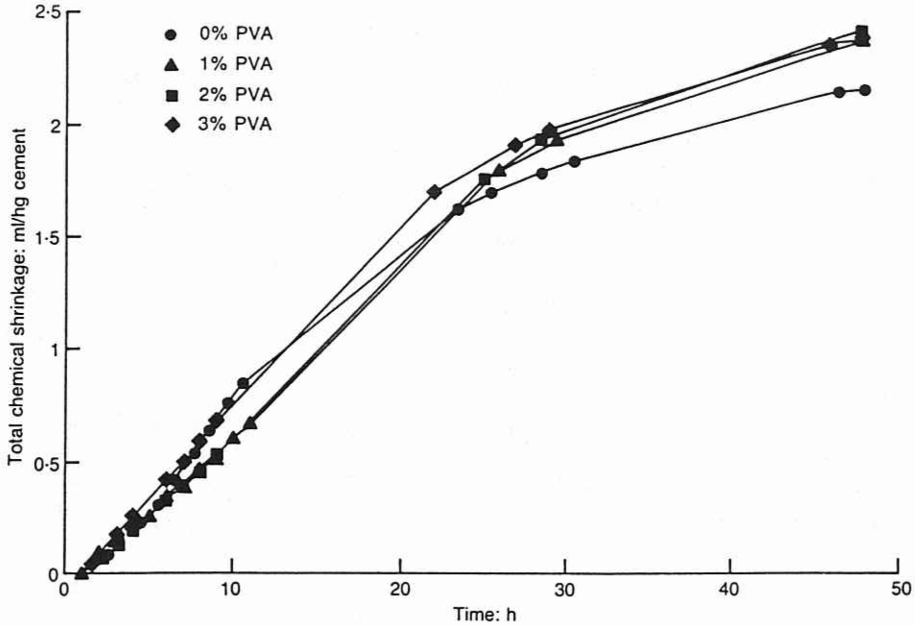

Fig. 4. The total chemical shrinkage of G cement slurries with w/c = 0·50 and various PVA additions at 1–48 h age

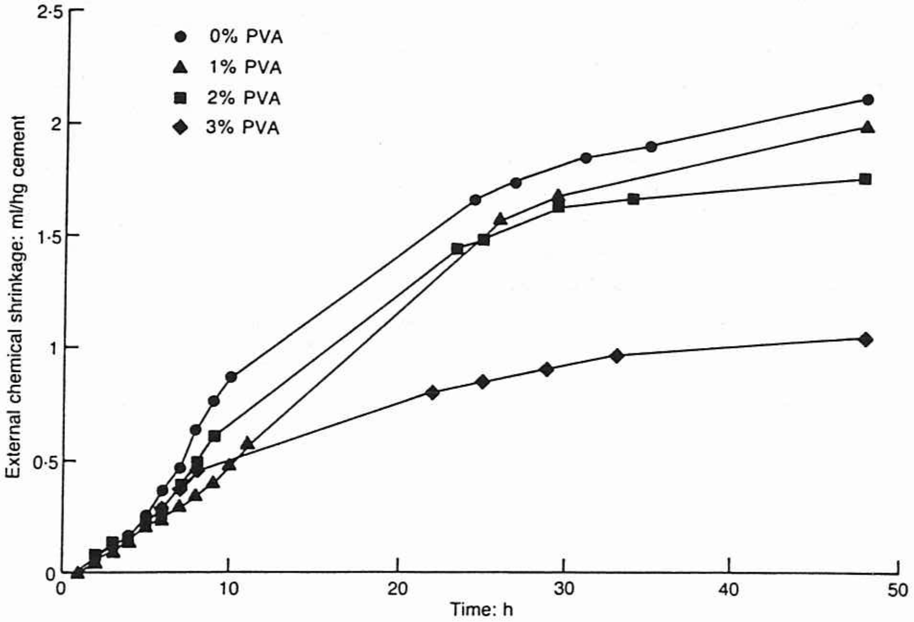

Fig. 5. The external chemical shrinkage of G cement slurries with w/c = 0·50 and various PVA additions at 1–48 h age

environment will increase, i.e. a stronger hydrate skeleton will be required in order to resist the forces. Increasing temperature may increase the flattening-out level of the external chemical shrinkage as well, since at higher temperatures the hydrate products are densified around the cement grains with a weaker skeleton between the particles. However, the effect of pressure and temperature on the external chemical shrinkage of G cement slurries is a topic for further research.

Sabins and Sutton[12] claimed that the formation of empty contraction pores accounts for 97·5%–99% of the total chemical shrinkage measured under realistic downhole conditions. Thus, external chemical shrinkage ranging from 0 to 0·43% was found[12] for various cement slurries based on G cement. In particular, when the cement sheet is in contact with a water-saturated formation, the external chemical shrinkage will be reduced due to the relief of the generated under-pressure by suction of formation liquid. The external chemical shrinkage measured by the condom method is a sealed situation with respect to water transportation, and hence a 'worst case'.

Conclusions

1. The chemical shrinkage, both total and external, of G cement slurries on hardening seems to be largely independent of the w/c in the first 48 h.

2. At 48 h, 20°C and atmospheric pressure, the total chemical shrinkage of a neat G cement slurry is 2·2 ml/100 g cement (2·6 vol.%), which corresponds to a degree of hydration of 35%.

3. The external shrinkage of a neat G cement slurry is about 1 ml/100 g cement or 1·2 vol.% at 20°C and atmospheric pressure.

4. Neither precipitated calcium carbonate ($\leq 15\%$) nor PVA ($\leq 3\%$) additions significantly influence the hydration rate of G cement with w/c = 0·50 in the first 48 h of curing, which implies that they may be used as additives to prevent bleed when external chemical shrinkage is being measured.

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