Effects of temperature and water-to-cement ratio on autogenous shrinkage of oil well cement

Xueyu Pang1,2,*, Lijun Sun2, Socorria Dos Santos Araujo2 and Yuhuan Bu1,2

1 Key laboratory of unconventional oil & gas development (China university of petroleum (east China)), ministry of education, Qingdao 266580, P. R. China; 2 School of petroleum engineering, China university of petroleum (east China), Qingdao 266580, P. R. China.

*Email: x.pang@upc.edu.cn

Abstract. The chemical shrinkage and corrugated tube test methods were used to study the shrinkage behaviour of Class G oil well cement with water-to-cement (w/c) ratios of 0.3 and 0.5, cured at temperatures from 15 to 60°C. The experimental results show that the typical linear shrinkage evolution curve of a cement slurry obtained by corrugated tube method have an obvious inflection point, beyond which the linear shrinkage increase is close to zero. The time at which the inflection point is observed decreases significantly with increasing curing temperature, but varies very little with w/c ratio. The inflection time also shows approximately linear correlation with the setting time of the cement (The two are almost equal for w/c =0.3). The degree of hydration corresponding with the initial and final setting time were estimated based on chemical shrinkage test results and the relationships between estimated volumetric bulk shrinkage and chemical shrinkage were analyzed.

1. Introduction

With the slow depletion of oil and gas resources in conventional reservoirs, oil and gas exploration are forced to develop in the direction of complex formations, which presents bigger challenges for the stability and safety of oil exploration. Cementing is one of the most important links in oil and gas well engineering. Its main function is to achieve zonal isolation between strata and establish efficient oil flow channels [1]. The quality of cementing determines the service life of oil and gas wells, and it could even determine the success or failure of an entire oil well [2]. Annular channeling is one of the main problems in the field of cementing engineering. The volume shrinkage of oil well cement will directly lead to the deterioration of the bonding strength of the first and second interfaces of the cement sheath [3-5]. This is the main cause of micro-cracks and fluid channeling in the annulus of the wellbore. Therefore, it is of great importance to develop an experimental method that can accurately quantify and characterize the volumetric shrinkage performance of oil well cement.

The hydration of cement is a complex chemical process that involves the reduction in volume when reactants (dry cement and water) are converted to resultants (hydration products). The total volume reduction is often referred to as the chemical shrinkage of cement, which can be reliably measured by a number of different test methods [6-8]. However, in engineering applications, it is the external bulk volume shrinkage that is detrimental to the structural integrity of cement-based materials. The bulk volume shrinkage is a lot more difficult to measure accurately compared to chemical shrinkage. API has reported four different methods to measure the bulk volume shrinkage of oil well cement,
including the annular ring-mold test, the membrane test, the cylindrical-sleeve test and the cement hydration analyzer test [9]. The first two methods have later been included in an API standard [10]. However, according to the review conducted by Reddy et al. [2], the agreements of test results obtained by these different methods are very poor. While the results of the annular ring-mold test appear to agree reasonably well with the ASTM method (ASTM C-151), the membrane test tends give significantly higher results, approaching the total chemical shrinkage values. Lura and Jensen had later found that the main source of error of the membrane test come from water uptake through the membrane [11-13].

Experimental measurement of the bulk volume shrinkage of cement-based materials is further complicated by the fact that cement slurry/paste experiences a phase transition from liquid to solid during the setting period. When the slurry is in a liquid state, all chemical shrinkage will be converted to bulk shrinkage (this is also known as the plastic shrinkage); With the development of a solid framework during setting, external bulk shrinkage will be significantly less than chemical shrinkage, and the majority of total volume reduction occurs inside the solid framework (often called internal shrinkage). API ring-mold test and ASTM C-151 are suitable methods for bulk shrinkage measurement of cement. However, with these methods, measurements can only be obtained after the cement had hardened and developed compressive strength. A standard corrugated tube test method is now available through ASTM [14], which allows the bulk shrinkage of cement to be continuously measured from the time of casting [15-17]. The corrugated tube provides minimum restraints to the dimension change of the specimen and prevent moisture exchange with the environment, avoiding most artifacts associated with other methods. Because the specimen is in sealed condition, the results obtained by this method is often called autogenous shrinkage, as it is primarily caused by self-desiccation inside the material.

Shrinkage is a complicated phenomenon in the cement hydration process, which is affected by many factors such as cement type, fineness, mineral composition, water-to-cement ratio (w/c), and curing conditions (temperature and pressure) [18-19]. This article focuses on studying the influences of w/c and curing temperature on the shrinkage behavior of oil well cement using chemical shrinkage and corrugated tube test methods. Comparisons between chemical shrinkage and bulk shrinkage can provide some interesting insights regarding the mechanism of cement shrinkage. Since autogenous shrinkage is defined as the bulk shrinkage of a sealed cement sample from the time of final setting, Vicat needle tests [20] were employed to determine the setting time of cement with different w/c ratios and cured at different temperatures.

2. Materials and methods

2.1. Materials and slurry preparation

The cement used in this study is an API Class G oil well cement, which is provided by Akesu cement plant, Xinjiang province, China. The compound composition of the cement as determined by quantitative XRD analysis is given in Table 1.

Table 1. Estimated main compound compositions (by mass percentage) of the cement.

| Compound | C₃S | C₂S | C₃A | C₄AF | Gypsum |
|----------|-----|-----|-----|------|--------|
| Quantity/% | 46.0 | 28.0 | 0.0 | 19.7 | 6.4 |

Table 2. Cement slurry formulation (% by weight of cement) and density of raw materials.

| Raw materials | Cement | Water | Dispersant | Defoamer | Diutan gum |
|---------------|--------|-------|------------|----------|------------|
| Density/(kg/m³) | 3.24×10³ | 1.0×10³ | 1.1×10³ | 0.96×10³ | 1.0×10³ |
| Formula 1 | 100 | 50 | 1 | 0.5 | 0.02 |
| Formula 2 | 100 | 30 | 1.5 | 0.5 | 0 |

2
Slurries were prepared according to standard API procedures [21] with water-to-cement (w/c) ratios of 0.3 and 0.5, respectively. A dispersant was used to tune the rheology of the slurries while a defoamer was used to remove the entrained air. A small amount of diutan gum was added to improve the stability of the slurry at higher w/c. The dispersant (BCD-210L) and defoamer (G603) used in this study were both provided by Tianjin PetroChina Boxing Technology Co., Ltd. The diutan gum was provided by CP Kelco (Shandong) Biological Co., Ltd. Detailed slurry compositions are shown in Table 2.

2.2. Vicat needle test
Vicat needle test was used to measure the initial and final setting time of the cement according to ASTM C191-18 [20]. The initial time of setting is the time elapsed between the initial contact of cement and water and the time when the penetration is measured or calculated to be 25 mm. The initial time of setting can be calculated by formula (1):

\[
\frac{H-E}{C-D} \times (C - 25) + E
\]

where, \(H\) (min) is the time for the first penetration less than 25 mm; \(E\) (min) is the time for last penetration greater than 25 mm; \(C\) (mm) is the penetration reading at time \(E\); \(D\) (mm) is the penetration reading at time \(H\). The final time of setting is the time elapsed between initial contact of cement and water and the time when the needle does not leave a complete circular impression in the paste surface.

2.3. Chemical shrinkage test
During this study, a self-designed experimental device was used to measure the chemical shrinkage of oil well cement at different curing temperatures. The device utilizes a syringe pump to continuously monitor the amount of water that is injected to a curing chamber filled with cement slurry. Such experimental test method is the same as those used in previous studies for oil well cement chemical shrinkage measurements and details of the experimental setup can be found in those references [7-8]. The inside of the curing chamber used here is shaped as a tapered cylinder with an average diameter of 55mm and a height of 250mm, rendering a total volume of about 600 mL. The curing chamber was pre-set to the target temperature to allow temperature stabilization before each test. A constant curing pressure of 5 MPa was applied during each test. Based on the results of previous studies, the influence of such a low pressure on cement hydration rate should be very minimal [7-8, 22].

2.4. Corrugated tube shrinking test

![Experimental set-up of the corrugated tube autogenous shrinkage test.](image)

Figure 1. Experimental set-up of the corrugated tube autogenous shrinkage test.

The corrugated tube shrinkage test device used in this article was designed according to ASTM C 1698-09 [14]. A picture of the experimental set-up is shown in Figure 1. The device consisted of three measurement channels to produce replicate results. The specific experimental steps are as follows: first, precondition the oil bath to the target temperature; secondly, pour the prepared cement slurry into corrugated tubes and seal the ends with plugs; finally, place the slurry-filled tube on the guide rail in the oil bath and continuously measure the length change of the tube using the dilatometer.
3. Test results and discussion

3.1. Settlement stability test results
It is necessary to determine the settlement stability of the cement slurry before the test to avoid test artifact caused by instability of the cement slurry. According to API standard [21], cylindrical cement samples with a diameter of 25 mm and a height of 150 mm were prepared and placed in a constant-temperature water bath for 24 hours. The cured samples were cut into four equal sections, with their densities determined according to the Archimedes' principle. No density difference was observed among different sections for each slurry formulation, indicating excellent slurry stability. The set cement density for formula 1 and formula 2 were $1.87 \times 10^3$ and $2.12 \times 10^3$ kg/m$^3$, respectively.

3.2. Vicat needle test results
The test method described in Section 2.2 was used to test the setting time of two cement slurries with different w/c ratios under different temperatures using the Vicat needle method. The specific test results are shown in Table 3.

| Temperature/℃ | Formula 1 (w/c=0.5) | Formula 2 (w/c=0.3) |
|---------------|----------------------|----------------------|
| Initial setting time/h | 7.9 | 6.1 | 5.0 | 7.7 | 4.7 | 4.5 |
| Final setting time/h    | 9.8 | 8.3 | 5.8 | 9.9 | 6.1 | 5.4 |

It can be seen from the test results that the setting time of two cement slurries decreases with the increase of curing temperature. Specifically, the initial setting time of the cement slurry was about 7.8 hours at 30°C and about 4.5-5 hours at 60°C; The final setting time was about 10 hours at 30°C and 5.4-5.8 hours at 60°C. The reduction in setting time with increasing temperature is mainly due to the fact that cement hydrates faster at higher curing temperatures. Comparing the test results of Formula 1 and Formula 2, it can be clearly observed that under the same curing temperature, the setting time of the cement slurry with lower w/c is generally shorter than that with higher w/c. This is because the cement slurry with a lower w/c has a higher solid volume fraction, and requires a relatively low degree of hydration to achieve setting. It is noted that the effect of w/c on the setting time is much smaller than the effect of curing temperature.

3.3. Corrugated tube shrinking test results
The linear shrinking test of formula 1 and formula 2 were completed under four different temperatures, namely 15°C, 30°C, 45°C and 60°C. Most of the time, the three measurement channels of the test device yielded at least 2 valid results per data set. It generally took about 20 minutes from the beginning of mixing cement slurry to the start of data collection. For consistency, the zero time of these experiments were set at the starting point of data recording.

Figure 2 and Figure 3 present the test results of the linear shrinkage evolution of the two cement slurries at 15°C. The test results show that both slurries show similar shrinkage behavior: the linear shrinkage of cement increases relatively rapidly during the early stage of cement hydration and then slows down rapidly after the cement sets. Correspondingly, the rate of linear shrinkage starts at a relatively high value and then gradually decrease to near zero over time. There is an obvious inflection point on the linear shrinkage evolution curve. The total linear shrinkage before the inflection point (plastic shrinkage) is in the range from 0.65% to 0.8% while the shrinkage increase after the inflection point is close to zero. For the purpose of consistency, the inflection time is defined by when the amount of shrinkage measured over a 5 minutes period first becomes less than 1 μm, which can be easily identified from the rate of shrinkage curve. At 15°C, the average inflection time is found to be 16.4 h for formula 1 (w/c =0.5) and 13.7 h for formula 2 (w/c =0.3). The inflection point in the linear shrinkage curve is likely to be caused by the setting of the cement, which provides a solid skeleton to the cement mixture to resist external shrinkage.
The time evolution curves of the linear shrinkage of the two cement slurries with different w/c at 30℃ are shown in Figure 4 and Figure 5. The overall shrinkage evolution profile is similar to the trend observed at 15℃. Specifically, the linear shrinkage evolution curves showed obvious inflection points after about 9-11 hours hydration, earlier than those observed at 15℃ due to faster setting. The inflection time agrees reasonably well with the Vicat needle final setting time measured at the same curing temperature (See Table 3). The amount of linear shrinkage measured before the inflection point (plastic shrinkage) is in the range between 0.4% and 0.55%, significantly smaller than that observed at 15℃. The shrinkage increase after the inflection point is approximately zero.
The time evolution curves of the linear shrinkage of the two cement slurries with different w/c at 45°C are shown in Figure 6 and Figure 7. Although some inconsistencies are observed between three different measurement channels for the low w/c slurry, the overall shrinkage evolution profiles are similar to the above test results. The total linear shrinkage values before the inflection points were about 0.2%-0.3%, smaller than those measured at lower temperatures. The average time at which the inflection points appeared is 5.9 h for formula 1 (w/c=0.5) and 5.8 h for formula 2 (w/c=0.3), respectively.

The shrinkage evolution behavior of the two cement slurries at 60°C are also similar to previous test results at lower temperatures, but the total linear shrinkage before the inflection point is further reduced to about 0.1%-0.14%. In order to get more direct comparisons of cement linear shrinkage behavior at different temperatures, the results of each data set were averaged and presented in Figure 8. It is obvious that the total linear shrinkage during the early stage before the inflection point decreases significantly with increasing curing temperature. According to previous studies, the linear shrinkage of cement during the early stage can be strongly influenced by the relative rigidity of the corrugated tube [17]. Therefore, the variation of early test results with temperature is likely to be associated with the rigidity change of the cement mixture and the corrugated tube at different temperatures. Figure 8 also shows that when the linear shrinkage is zeroed at the final setting time of cement based on Vicat needle test, the total amount of autogenous shrinkage at all curing temperatures is near zero after final setting with the exception of formula 2 (w/c=0.3) at 30°C. These measured shrinkage values are lower compared to ordinary Portland cement used in the construction industry [23], which may be explained by the differences in cement composition, considering that the Class G oil well cement used here contains no C₃A.

**Figure 8.** Summary of average linear shrinkage and autogenous shrinkage at different temperatures.

(dotted lines: w/c=0.3, solid lines: w/c=0.5)

| w/c  | 0.3 | 0.5 |
|------|-----|-----|
| Temperature  | 15°C | 30°C | 45°C | 60°C | 15°C | 30°C | 45°C | 60°C |
| Channel 1 | 12.63 | 11.05 | 5.79 | 5.24 | 16.13 | 9.59 | 5.98 | 4.8 |
| Channel 2 | 13.65 | 10.95 | 5.83 | 5.38 | 16.67 | 8.63 | 6.08 |  |
| Channel 3 | 14.94 | 10.13 | 5.84 | 5.73 | 9.36 | 5.61 |  |  |
| Average  | 13.74 | 10.7 | 5.8 | 5.45 | 16.4 | 9.2 | 5.9 | 4.8 |
| COV     | 8.4% | 4.7% | 0.5% | 4.6% | N/A | 5.5% | 4.2% | N/A |

Table 4 summarizes the observed inflection time on the shrinkage evolution curves of the two under different curing temperatures. The results are relatively consistent among the three measurement channels, with the coefficient of variation (COV) in each data set less than 8.4%. All tests results show that the inflection point appears earlier at higher curing temperature. This is mainly due to the higher hydration rate at higher curing temperature, which in turn causes the cement to form a network structure earlier, and ultimately inhibits external shrinkage. Under the same curing temperature,
the inflection time of cement slurry with different w/c is not much different. The results suggest that the effect of curing temperature on the inflection time is significantly higher than w/c.

3.4. Discussions of test results
Comparing the data in Table 4 and Table 3, one can find an interesting phenomenon that the final setting time and the inflection time correlate positively for the same slurry formulation at the same curing temperature. Figure 9 more intuitively shows the relationship between the average inflection time and the final setting time. It can be seen that the setting time of the slurry with w/c=0.3 is approximately equal to the inflection time, while the setting time of the slurry with w/c=0.5 is slightly longer than the inflection time. The correlations between the two parameters are approximately linear for both w/c ratios, suggesting that one may use one data set to estimate the other one. Setting and linear shrinkage of cement are both closely related to the degree of cement hydration. According to the definition of final setting, cement slurry is converted from plastic fluid to solid after a period of hydration. Assuming the cement can continuously imbibe water from the environment to remain fully saturated at all times, theoretically there would be no external bulk shrinkage. However, under sealed condition, the internal volume reduction as a result of chemical shrinkage will exert a vacuum force on the solid skeleton of the cement mixture, leading to autogenous shrinkage. This study revealed that the autogenous shrinkage of the oil well cement slurries investigated here is approximately zero, suggesting the vacuum force is too small to generate any appreciable strain on the set cement.

![Figure 9. The relationship between inflection point time and final setting time.](image)

![Figure 10. The effect of curing temperature and w/c on cement chemical shrinkage (dotted lines) and bulk shrinkage (solid lines) of oil well cement (bulk shrinkage is calculated based on linear shrinkage test results assuming uniform shrinkage in all directions).](image)
much less than the chemical shrinkage. The crossover generally occurs at or before the final setting time of the cement.

Using the compound composition of the cement presented in Section 2.1 along with the empirical function proposed by Pang et al. [8], the ultimate chemical shrinkage of the cement at fully hydrated condition under 25℃ curing temperature may be estimated. The ultimate chemical shrinkage at other temperatures may be estimated by assuming a linear reduction rate of 0.6%/℃ with the increase of temperature [6]. Based on the actual chemical shrinkage test results obtained in this study, the degree of hydration of the cement at the initial and final setting time may be derived. Table 5 shows the calculated degree of hydration corresponding with the time of set at different curing temperatures. It appears that the degree of hydration at both initial set and final set increases significantly with increasing curing temperature. A previous study has reported that the degree of hydration of Class H cement with w/c=0.35 is approximately 3.88±0.38% at the initial setting time under different curing temperatures (from 10 to 60℃) [24]. The different values obtained here may be associated with different experimental methods as well as different cement compositions.

Table 5. Calculated degree of hydration at time of set under different curing temperatures.

| Temperature/℃ | CS$_0$/mL/100g | w/c=0.5 | w/c=0.3 |
|---------------|----------------|---------|---------|
|               |  α$_I$/% |  α$_F$/% |  α$_I$/% |  α$_F$/% |
| 30            | 10.8    | 19.9    | 10.6    | 22.6    |
| 45            | 25.3    | 37.9    | 9.2     | 24.8    |
| 60            | 28.8    | 37.1    | 21.9    | 32.5    |

$^a$ α$_I$ is the calculated degree of hydration at the time of initial set;
$^b$ α$_F$ is the calculated degree of hydration at the time of final set;
$^c$ CS$_0$ is the estimated ultimate chemical shrinkage at complete hydration.

4. Conclusions
The influences of w/c ratio and curing temperature on the shrinkage behavior of Class G oil well cement were investigated using chemical shrinkage and corrugated tube test methods. The following conclusions may be drawn from this study:

1. The Vicat setting time of cement slurries with both w/c ratios (0.3 and 0.5) decreases with the increase of curing temperature; Under the same curing temperature, the setting time of the cement slurry with lower w/c is generally slightly shorter than that with higher w/c.

2. The linear shrinkage of cement measured by the corrugated tube method is relatively high during the plastic stage (i.e. before setting), but reduces to near zero during the autogenous shrinkage stage (i.e. after setting); the plastic shrinkage measured by corrugated tube method decreases significantly with increasing curing temperature.

3. The significant change in linear shrinkage rate of cement at time of set produced an obvious inflection point on the shrinkage test curve, which correlates very well with the setting time measured by Vicat needle test method especially for lower w/c ratio. The w/c ratio seem to have very little influence on the time of the inflection point.

4. The degrees of cement hydration at initial and final setting time are estimated to be about 10% and 20%, respectively, at 30℃ based on chemical shrinkage test results, which seem to increase significantly with increasing curing temperature.

Acknowledgements
The authors gratefully acknowledge the financial support provided by National Natural Science Foundation of China (Grant No. 51974352).

References
[1] Smith D K 1990 Cementing, SPE Monograph series 4
[2] Reddy B R, Xu Y, Ravi K, et al 2007. Drilling & completion 24(1) 104-114
[3] Parcevaux P A, Sault P H 1984. SPE 13176 Annual technical conference and exhibition 1-7
[4] Justnes H, Van Loo D, Reyniers B, et al 1995. Adv. Cem. Res. 7 85-90
[5] Lyomov S K, Backe KR, Skalle P, et al 1997. The petroleum society 1-7
[6] Pang X, Bentz D P, Meyer C, et al 2013. Cem. Concr. Compo 39 23-32
[7] Pang X, Meyer C, Darbe R, et al 2013. ACI Mater 110(2) 137-148
[8] Pang X, Meyer C 2012. ACI Mater 109(3) 341-352
[9] API TP 1997, Shrinkage and Expansion in Oilwell Cements, first edition, American Petroleum Institute, 10TR2 (58 pp.)
[10] ANSI/API Recommended Practice 2015, Recommended Practice on Determination of Shrinkage and expansion of Well Cement Formulations atmospheric Pressure, first edition, American Petroleum Institute, reaffirmed, 10B-5(13 pp.)
[11] Lura P, Jensen O M, Van Breugel K 2003. Cem. Concr. Res. 33(2) 223-232
[12] Jensen O M, Hansen P F 2001. Cem. Concr. Res. 31 1859-1865
[13] Lura P, Jensen O M 2007. Mater. Struct. 40(4) 431-440
[14] ASTM 2019, Standard Test Method for Autogenous Strain of Cement Paste and Mortar, ASTM International, C1698-19 (8 pp.)
[15] Snoeck D, Jensen OM, De Belie N 2015. Cem. Concr. Res 74 59-67
[16] Bao Y, Meng W, Chen Y, et al 2015. Mater. Lett 145 344-346
[17] Tian Q, Jensen O M 2009. Journal of the Chinese Ceramic Society 37(1) 39-45
[18] Brooks J J, Cabrera J G 1998 Factors affecting the autogenous shrinkage of silica fume high strength concrete. In: Proceedings of international workshop on autogenous shrinkage of concrete, Hiroshima, Japan. Japan: Japan Concrete Institute; 185-192
[19] Chu I, Kwon S H, Amin M N, et al 2012. Constr Build Mater. 35 171-182
[20] ASTM C 2019. Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle, ASTM International, 191-19 (8 pp.)
[21] API Recommended Practice 2013, Recommended Practice for Testing Well Cements, second edition, American Petroleum Institute, 10B-2(111 pp.)
[22] Pang X, Jimenez W C, Iverson B J 2013. Cem. Conc. Res. 54 69-76
[23] Wyrzykowski M, Hu Z, Ghourchian S, et al 2017 Mater. Struct. 50 57
[24] Zhang J, Weissinger E A, Peethamparan S, et al 2010 Cem. Conc. Res. 40(7) 1023-1033