

SETTING SHRINKAGE MEASUREMENT DURING CEMENT HYDRATION

Stefan Kuiper*, Geert Wams, Alexandra Spies
Almatix B.V., Rotterdam, The Netherlands

Dagmar Schmidtmeier, Sebastian Klaus, Andreas Buhr
Almatix GmbH, Frankfurt/Ludwigshafen, Germany

Jerry Dutton
Stourbridge, United Kingdom

4

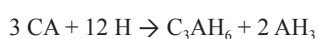
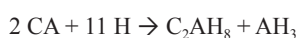
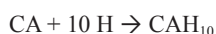
ABSTRACT

The shrinkage behaviour of castables during hydration was investigated. The shrinkage curves and exothermal measurements were used to determine the densification, stiffening and hydration stages. The shrinkage rates during hydration of castables with different concentrations of calcium aluminate cement were compared. The more cement that was used, the faster the shrinkage achieved. When retarding the castable with a higher ADS/ADW ratio the shrinkage rate was decreased.

INTRODUCTION

Volume shrinkage during the setting of refractory castables is inherent because the density of the total system – calcium aluminate phases plus water – increases when calcium aluminate hydrates are forming during the reaction of cement with water. [1] This setting shrinkage has a major impact during the production of pre-cast shapes, for example when internal moulds such as cones, are used in the production of well blocks. Even relatively small shrinkage causes a clamping of the inner mould, which makes it difficult or impossible to remove if the setting has progressed too far. In the worst case, cracking can occur which only becomes visible after the drying of the pre-cast shapes. Therefore the removal of the inner mould at the right time is a challenging task, because sufficient strength must be developed to keep the material shape and to avoid slumping, but also the setting must not proceed too far to avoid clamping. It is therefore important to understand the development of shrinkage.

In the early stage the castable is still flowing and volume shrinkage is caused by densification and de-airing of the castable. During the hydration of calcium aluminate (CA) phases water is incorporated into a crystalline structure. The solid fraction is increasing by weight and volume, while the low density liquid water content is decreasing. The total volume of the CA phase and water is higher than of the hydrated products. This density change causes a shrinkage for each gram of hydrated CA to CAH_{10} , C_2AH_8 or C_3AH_6 of 0.23 ml, 0.22 ml and 0.27 ml respectively. [2]



In castables the chemical shrinkage only partly causes a volume change of the piece. A relative large amount of chemical shrinkage results in internal porosity. Chemical shrinkage could be measured by water pycnometry or dilatometry according to ASTM C 1608. [3] With these measurements the total vol-

ume shrinkage is determined including internal porosity. Measuring the chemical shrinkage by volume changes of a cement paste by water pycnometry or dilatometry cannot be correlated to the shrinkage of a cast piece, because the increased internal porosity does not contribute to dimension changes. [4]

In order to determine the potential of clamping of the inner moulds and related internal stresses, the dimension changes of the piece have to be measured. Dimension changes are relatively small and therefore large pieces are needed to determine shrinkage using normal equipment or very accurate measurement systems involving laser technology. Schleibinger Geräte developed a shrinkage measurement device [5-6] based on a cone. Shrinkages in all dimensions are reflected in the height of the piece due to the cone shaped piece. The height difference can be measured with an accuracy of 0.5 μm by using a laser.

Tab. 1: Density and water content of mineral phases

Mineral	Density [g/ml]	Percentage water [wt%]
CA	2.98	0
CAH_{10}	1.72	53
C_2AH_8	1.95	40
C_3AH_6	2.52	29
AH_3	2.42	45
H	1.00	100

EXPERIMENTAL PART

Sample preparation

The castables were prepared in a Hobart mixer. The solid components (4 kg total) were added and dry mixed for 1 minute. After 1 minute the water was added and the mix wet mixed for a further 4 minutes. The castable (1.5 kg) was poured into a plastic box and a thermocouple wire added to measure the exothermal reaction. The Schleibinger cone was filled to a height of 12 cm. The half cone angle was 30°. All experiments were performed in a temperature controlled laboratory (20°C \pm 1°C).

The castable recipes are shown in Table 2. All measurements on the recipes were repeated 4 times and averages taken for further data analysis.

The calcium aluminate cement (CAC) percentage was replaced by -45 μm Tabular when higher or lower CAC concentrations were used, because the particle size distribution of both products is similar. A CAC free castable was prepared by modifying the standard recipe when all CAC was replaced by -45 μm Tabular.

To have a good workability in the high CAC containing castable, the water demand had to be slightly increased.

Tab. 2: Castable recipes

	Standard	Low CAC	High CAC	Retarded
wt. %				
Tabular				
3 – 6 mm	25	25	25	25
1 – 3 mm	15	15	15	15
0.5 – 1 mm	11	11	11	11
0.2 – 0.6 mm	6	6	6	6
0 – 0.2 mm	12	12	12	12
– 45 µm	9	<u>11.5</u>	4	9
Reactive alumina				
CTC 50	17	17	17	17
Cement				
CA-14 M	5	<u>2.5</u>	<u>10</u>	5
Dispersing alumina				
ADS 3	0.3	0.3	0.3	<u>0.7</u>
ADW 1	0.7	0.7	0.7	<u>0.3</u>
Water	4.5	4.5	<u>4.7</u>	4.5

RESULTS AND DISCUSSION

Exothermal measurements

In the exothermal curve three stages could be determined. After mixing the temperature increased to about 25°C. The mix then cools down slowly. At this point the mix is self-flowing. After this first stage a small peak of about 0.5°C could be observed. For the standard castable this starts 62 minutes after mixing. This peak is combined with a stiffening of the mix. No real strength is obtained yet. Pieces at this time can be easily damaged when external forces are applied. Hydration takes place in the last stage. During this stage hydrates are formed and strength is obtained. For the standard recipe this started at 114 minutes and the maximum temperature was reached after 200 minutes. Table 3 shows the exothermal data for all castables.

The three stages could be observed in all castables. In Figure 1 the exothermal curves are plotted for the castables with different CAC concentrations. Fast setting times are obtained when 10% CAC was used, the maximum temperature is also higher, 33.3°C compared to 26.8°C. When 2.5% CAC was used the setting times were retarded and the maximum temperature reduced to 24.6°C.

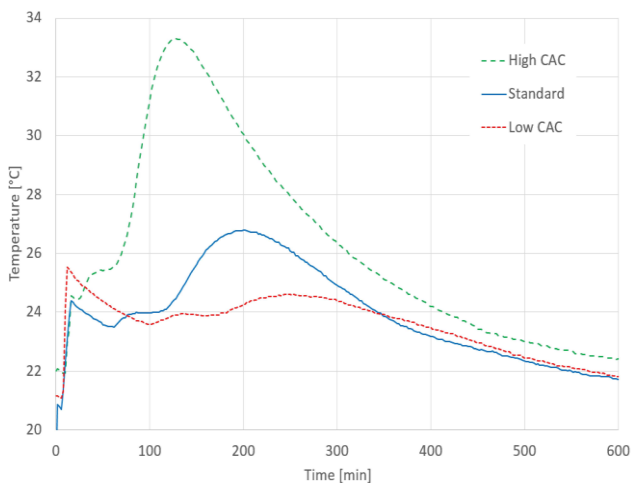


Fig. 1: Exothermal curves for castables with 2.5%, 5% and 10% CAC.

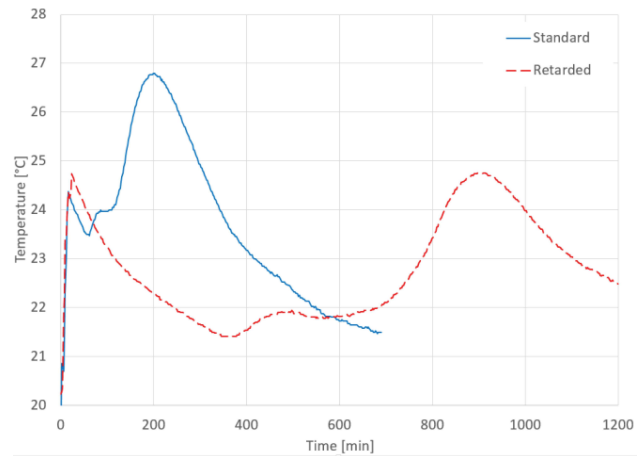


Fig. 2: Exothermal curves of standard and retarded castables.

The time difference between the start of hydration and the time the maximum temperature was reached is similar for all concentrations (2.5%, 5% and 10%) – (84, 86 and 70 minutes respectively). This means that the peak characteristic is almost identical, but that the intensity changed with the concentration of CAC.

The setting was modified by using an ADS/ADW ratio of 0.7/0.3 instead of 0.3/0.7 for the standard recipe. As shown in Figure 2, the start of hydration was retarded to 668 minutes instead of 114 minutes. The maximum temperature occurred at 908 minutes compared to 200 minutes. It takes 240 minutes to reach the maximum temperature from the start of hydration. The shape of the hydration peak is broadened and as a result the maximum temperature was lowered to 24.7°C.

Tab. 3: Exothermal data

	Standard	Low CAC	High CAC	Retarded
Start 1st peak [min]	62	104	24	384
Hydration start [min]	114	170	60	668
Temperature max. [min]	200	254	130	908
Temperature max. [°C]	26.8	24.6	33.3	24.7

Shrinkage measurements

In the shrinkage curve the three stages can also be identified. In the first stage the castable is still self-flowing and densification takes place due to rearrangement of particles and degassing. This is reflected by a relatively high shrinkage rate. In the second stiffening stage the particles are less mobile and rearrangement of particles takes place more slowly and therefore the shrinkage is slowed down. In the final stage chemical shrinkage due to hydration takes place which could be seen in an accelerated shrinkage. When this shrinkage stops, the volume of the piece does not change further.

In order to clarify the densification stage, the shrinkage of a CAC free castable was measured. The shrinkage curve was plotted together with the curves of standard and retarded castables and is shown in Figure 3. The shrinkage continued for 35 hours and levelled out at 32%. This shrinkage is purely caused by densification and de-airing. For CAC containing castables the same densification profile is observed, but stops as soon as the stiffening and hydration occurs. Greater densification is achieved when the setting time is more retarded, because the self-flowing stage is extended.

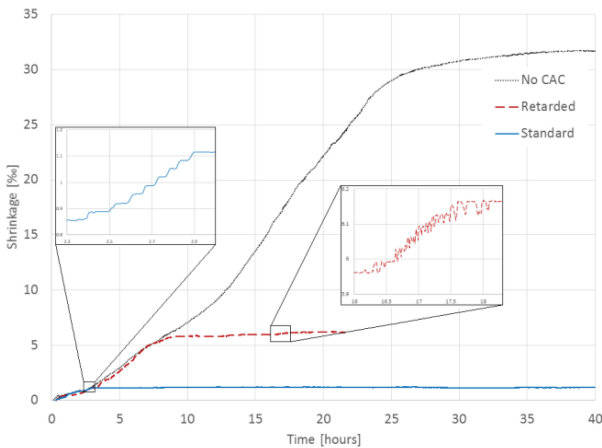


Fig. 3: Shrinkage curves of no CAC, standard and retarded castables

During hydration the castable is hardened and stresses formed during shrinkage cannot relax and will create internal stresses. This is different when compared to the densification stage where forces can relax by particle rearrangement. The volume change during hydration is the critical factor for internal stresses and clamping of inner-moulds. In order to compare the shrinkage caused by hydration of castables with different setting times the origin of the shrinkage curves was set to the start of hydration. The shrinkage curves of the castables with different CAC contents were plotted in Figure 4 with the start of hydration as the origin. For the standard recipe the shrinkage levelled off at 0.22‰ after 32 minutes. What could be noticed is that the shrinkage stopped while the exothermal measurement still showed heat development. This is indicating that the aggregate framework is stabilised and fixed by the hydrates formed. The further hydration which takes place should result in porosity, due to the continuing chemical shrinkage. Total shrinkages of about 0.23‰, 0.22‰ and 0.29‰ were reached when using 2.5%, 5% and 10% CAC respectively. The total shrinkage is not proportional to the CAC concentration. This indicates that the formation of the aggregate framework is the main determining factor for total shrinkage. The shrinkage rate is determined by the amount of CAC used. When 2.5% CAC is used, the shrinkage rate slowed down and the shrinkage time is 163 minutes, while the castable with 10% CAC shrinks within 21 minutes. Lowering the CAC concentration could help to extend the time window to remove the inner mould, but would also lower the final strength levels.

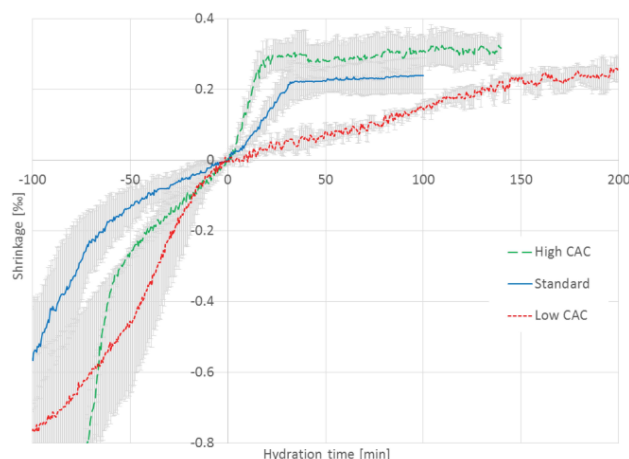


Fig. 4: Hydration shrinkage curves of 2.5, 5 and 10% CAC containing castables

Tab. 4: Shrinkage data

	Standard	Low CAC	High CAC	Retarded
Final shrinkage [‰]	0.22	0.23	0.29	0.26
Shrinkage time [min]	32	163	21	94

Retarding the CAC hydration by different ratios of ADS/ADW is lowering the shrinkage rate as can be seen in Figure 5. This can be explained by the hydration rate. In the exothermal curve it can be seen that it takes 240 minutes from the start of hydration to reach the maximum temperature. This means that a larger demoulding time window e.g. for an inner core in a well block, could be achieved by retarding the setting, but the time needed to demould the entire well block would also be increased.

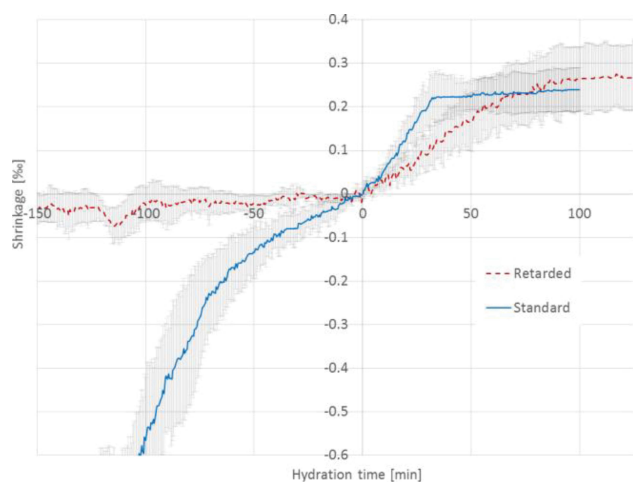


Fig. 5: Hydration shrinkage curves standard and retarded castables.

The Young's modulus of concretes is between 20 and 30 GPa. [7] The pressure needed to deform a concrete piece by 0.2‰ is 4 – 6 MPa according to equation 1. This indicates that the internal stresses can be significant around an inner mould with shrinkages of 0.2‰. This is in line with the fact that a hammer is required to remove the inner cones even if it is done at the right time. These stresses can also explain the crack formation at later stages in the process of the pre-cast shape production if the inner core was removed too late when shrinkage was already too high.

Equation 1
$$E = \frac{\sigma(\epsilon)}{\epsilon}$$

In equation 1, E is the Young's modulus, σ is the tensile stress and ϵ is the strain

CONCLUSION

Shrinkage of castables is occurring in three stages, the densification, stiffening and chemical shrinkage caused by hydration. Shrinkage by densification does not contribute to difficulties with the inner mould of pre-cast shapes because the castable is still plastic. During the stiffening stage the flowability stops and with that the densification. During hydration the volume of the piece shrinks until the aggregate structure is stabilised. The shrinkage rate is impacted by the concentration of CAC used in the castable and also by the ADS/ADW ratio.

REFERENCES

- [1] Gosselin C, PhD Thesis Microstructural Development of Calcium Aluminate Cement Based Systems with and without Supplementary Cementitious Materials, 2009
- [2] Hart LD, Alumina Chemicals Science and Technology handbook, ISBN 0-916094-33-2, page 175-180
- [3] ASTM C 1608. Standard test method for chemical shrinkage of hydraulic cement paste. West Conshohocken: American Society for Testing and Materials; 2007.
- [4] Zhang T, Gao P, Luo R, Guo Y, Wie J, Yu Q, Measurement of Chemical Shrinkage of Cement Paste: Comparison Study of ASTM C 1608 and an Improved Method, Construction and Building Materials 48, 2013, page 662-669
- [5] Greim M, Teubert O, Appliance for detecting initial expansion and shrinkage behaviour of building materials based on contactless measurement of change in filling level of container of fresh material specimens until set, Patent DE 10046284, 2011
- [6] www.schleibinger.com
- [7] Taylor HFW, Cement Chemistry, 2nd edition, ISBN 0-7277-2592-0, 1997, page 256