

THE INFLUENCE OF CURING CONDITIONS ON CEMENT HYDRATION AND STRENGTH

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ABSTRACT

The ambient conditions such as temperature, humidity, and a covering of the cast material can have an influence on the strength development of calcium aluminate cement bonded refractory castables. This is important for both, laboratory testing and installation of refractory castables in practice. The paper discusses results obtained in calorimetric testing of cement test grog and of castable testing under practical laboratory conditions with different cement content and additives in the test castables. Besides the well-known influence of ambient temperature on the hydration and strength development also the covering of the material can have a significant influence on the strength development during curing. Systematic differences are observed between conventional castables, low cement castables, and ultra-low and no cement castables. The water to cement ratio respectively binder to cement ratio is responsible for these differences. Recommendations are made for the curing of the different castables.

INTRODUCTION

Setting behavior and strength development of cement-bonded castables are key properties tested during the development work and quality control by most refractory producers.

Whereas no common standard does exist for testing of calcium aluminate cement, the curing conditions for refractory, cement-bonded castables are described in the standard ISO 1927-5. The importance of consistent ambient temperature and humidity during curing of the samples is emphasized to ensure a good repeatability of the results. The influence of curing conditions on setting behavior and strength development is known to refractory experts though in laboratory practice a variety of ways can be found to meet these requirements.

By comparison of the different methods for different types of concrete, the influence of the curing conditions on the green strength development is shown.

IMPACT OF AMBIENT TEMPERATURE ON SETTING AND STRENGTH

When considering the reliability of testing not only is the test mixture of importance, but also the ambient temperature. Calorimetric measurements of 80% tabular alumina and 20% cement, which are, for standard tests at the University of Erlangen, performed at 23°C, were also tested at 20°C to investigate the impact of a small temperature variation on the cement hydration. The heat flow curves for both temperatures are shown in Fig. 1. The reduction of ambient temperature of only 3°C during the hydration test has a clear retarding effect of about six hours on the main hydration peak, although the shape of the curve does not change. This indicates that the same reaction kinetics take place during the main reaction.

A similar trend has been observed in a series of tests performed in the Almatis laboratory where setting behavior of different castables was tested at 20°C ambient temperature in the laboratory vs. 20°C in the climate cabinet. When compared to the curing process in an air-conditioned room, where the heat released results in an overall heating of the test block, the heat released in the climate cabinet is dissipated immediately and the exothermic reaction is

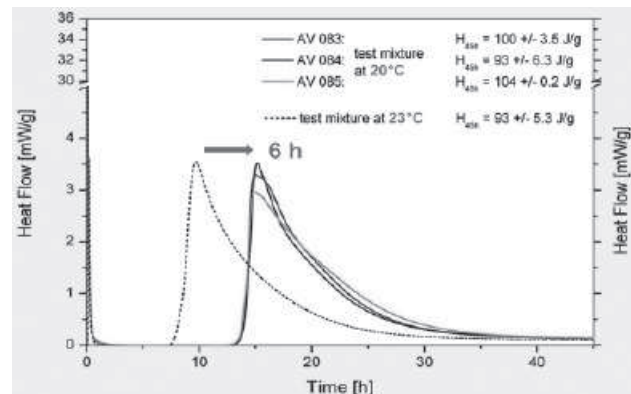


Fig. 1. Hydration of 20% CA-14 and 80% tabular alumina filler at 20°C vs. 23°C ($w/s=0.275$)

suppressed and also retarded. The exothermic profiles of two different low cement castables cured at 20°C in the room and in the climate cabinet are given in Fig. 2. The temperature increase right at the start is due to heat developed in the castable during the mixing by friction. As the cement hydration is very sensitive, even under well-defined conditions, the repeatability will become worse

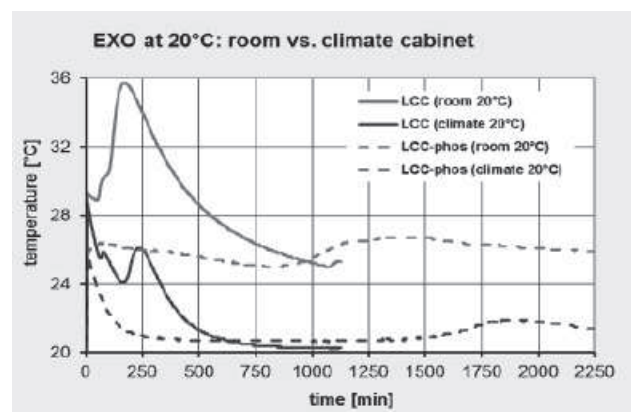


Fig. 2. Exothermic reaction of two low cement castables at 20°C in the laboratory and in a climate cabinet: later hydration in the climate cabinet

under less controlled ambient temperatures in the laboratory, for example without air conditioning.

It is well known that not only is the setting behavior of refractory castables impacted by the curing temperature but also is the strength development. This is because the strength depends on the degree of hydration achieved during curing.

Single measurements of tabular alumina low cement castable illustrate the correlation of the exothermic setting curve and the strength development (Fig. 3) and also the ultrasonic setting curve and the strength development (Fig. 4). The strength development starts between the first and the second rise of the exothermic curve (EXO start 1 and 2) simultaneously with the increase in ultrasound velocity.

Low temperature curing has a negative effect on the strength development because of two effects. The cement hydration is retarded at low temperatures and therefore less strength develops. Also the calcium aluminate hydrates formed during hydration at low temperatures contain more water and have a lower densi-

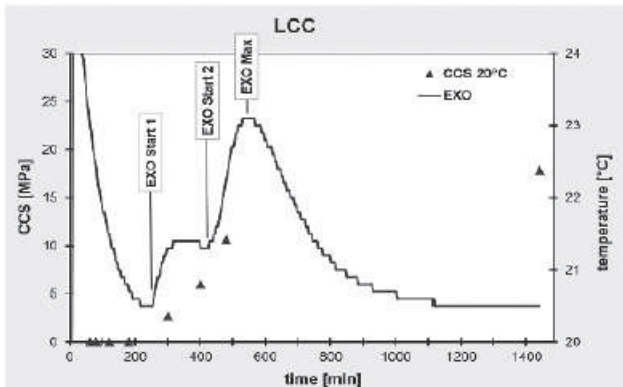


Fig. 3. Correlation of the exothermic reaction and strength development at 20°C of a low cement castable

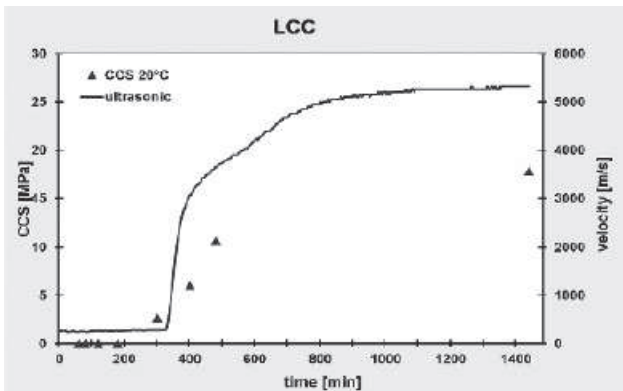


Fig. 4. Correlation of the ultrasonic setting and strength development at 20°C of a low cement castable

ty when compared to hydrates formed at higher curing temperatures^[1-3]. Previous investigations from Buhr et al.^[4] on strength development at 5 and 20°C demonstrate that calcium aluminate cements inherently develop less strength during curing at low ambient temperatures. This is shown in Fig. 5.

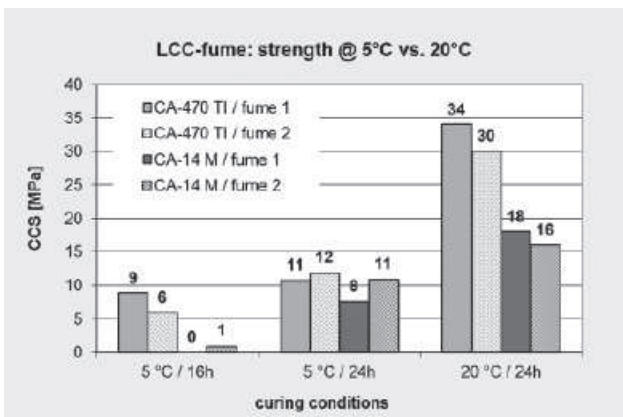


Fig. 5. Cold crushing strength of test castables after curing at 5 and 20°C

IMPACT OF CURING CONDITIONS ON STRENGTH

Strength development during curing is an important consideration during the development work and quality control of refracto-

ry castables in addition to the rheological properties during mixing and placement. The significant influence of temperature on the strength development has been discussed before. In addition, the samples may be covered during curing or be exposed to air drying. The impact of different curing methods was investigated for six test castables based on tabular alumina aggregate with cement contents of 0 – 15%.

Test castables

The conventional castable (CC) contained 15% CA-25 C. Three low cement castables were selected, containing 5 – 6% CA-14 S or CA-270. Two of the three were pure alumina castables – one containing ADS/W (LCC), the other with sodium polyphosphate (Budite 8H) and sodium citrate as additives (LCC-phos). The third was a silica fume containing mix with M-ADS/W (LCC-fume). The ultralow cement castable was a silica fume free mix containing 3% CA-270 (ULCC). For the no-cement formulation 3% Al-phabond 300 was used as the hydratable alumina binder (NCC). The composition of the test castables is given in Tab. I.

Tab. I. Composition of test castables

		CC	LCC	LCC-phos	LCC-fume	ULCC	NCC
		%	%	%	%	%	%
T60/T64	coarse	70	69	74	74	69	75
	fine	5	9	9	8	11	9
Almatis calcined alumina		10	-	-	-	-	-
Almatis reactive alumina		-	17	11	10	17	13
Silica fume Elkem 971U		-	-	-	3	-	-
Binder	CA-25 C	15	-	-	-	-	-
	CA-14 S	-	-	6	5	-	-
	CA-270	-	5	-	-	3	-
	AB 300	-	-	-	-	-	3
Additives	ADS/W	-	1.0	-	-	1.0	1.0
	M-ADS/W	-	-	-	1.0	-	-
	Budite 8h	-	-	0.05	-	-	-
	Na-citrate	-	-	0.03	-	-	-
Water		7.8	4.5	5.5	4.3	4.5	4.5

The different castables were wet mixed in 5 kg batches using a Hobart A200 planetary mixer at speed 1 for 4 minutes. Test bars were cast immediately after mixing and cured under different conditions for 24 hours and in selected cases for 48 hours. For the curing process the test bars were stored as follows:

- Exposed to air drying: The molds with the test bar were stored in the laboratory at 20°C for 24 hours without a cover.
- Covered: The mold's with the test bar were stored in the laboratory at 20°C for 24 hours and were covered with a Plexiglas-plate.
- In a plastic bag: The molds with the test bar were stored in a securely closed plastic bag in the laboratory at 20°C.
- In the climate cabinet: The mold's with the test bar were stored in a climate cabinet at 20°C and 90% relative humidity for 24 hours.
- According to European standard DIN-ISO 1927 part 1-8: The molds with the test bar were stored in a climate cabinet at 20°C and 90% relative humidity for 24 hours. The bars were then de-molded and stored for a further 24 hours in the climate cabinet under the same conditions.

Cold crushing strength was determined after 24 hours. The cured strength after 48 hours was also measured for the castables CC, LCC-phos, and NCC. In addition to the cured strength, the weight loss of the castable bars during curing was determined after 2, 4,

6, 8 and 24 hours. This data was used later for calculation of the water/cement (w/c) ratio and water/Alphabond-binder (w/b) ratio after the different curing steps.

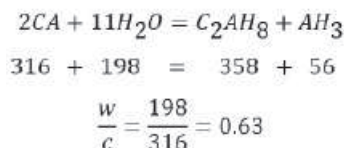
Critical water/cement ratio

In order to achieve the desired strength development during curing sufficient water should be provided for the cement hydration. In technical systems with coarse aggregates, fine fillers, and cement, sufficient water is also needed for the required flow behavior and placing properties of the mix. However, too high water demands are disadvantageous for the refractory properties in use. The minimum water demand required for a theoretically complete cement hydration can be calculated and is known as critical water/cement ratio.

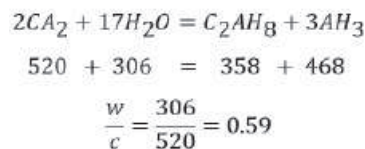
The critical water/cement ratio depends on the nature of the hydrates formed.^[5] Scrivener et al. state a critical water/cement ratio of about 0.7 for calcium aluminate cement containing about 50% CA for low temperatures when CAH_{10} is present, and 0.35 for high temperatures when C_3AH_6 and gibbsite (AH_3) are formed. As curing trials for this test series were performed at 20°C the critical water/cement ratio was calculated for C_2AH_8 and AH_3 , which can be assumed to be the dominant hydrate phases formed in this temperature range. Here, a critical w/c ratio of about 0.6 for a theoretically complete cement hydration is obtained from the calculation below.

(C = CaO, A = Al_2O_3 , H = H_2O ; molecular weight g/mol):

Calculation for CA:



Calculation for CA_2 :



RESULTS AND DISCUSSION

Fig. 6 shows the w/c and w/b ratios for the different test castables and curing methods over curing time of 24 hours. The red area indicates the critical w/c ratio which was set at 0.5-0.6 based on the calculation above and taking into account that complete cement hy-

dration in technical systems normally does not occur. The critical water/Alphabond ratio was also set at 0.5-0.6. Complete AH_3 formation would require $w/b = 0.53$, but at 20°C an amorphous aluminum hydrate phase is formed which may contain more water when compared to crystallized AH_3 .

For all castables the decrease of water/binder ratio during curing is lowest for test bars cured with a cover or packed in a plastic bag and highest when stored exposed to air drying.

In the case of the CC mix with 15% cement the curing process has already started at the critical w/c ratio. During curing without cover, when exposed to air drying and also in the climate cabinet water evaporates and is no longer available for cement hydration. The w/c ratio of the CC has already fallen below the critical w/c ratio after 6 – 8 hours curing.

The low cement castables with 5 – 6% cement start at a higher w/c ratio of 0.85 – 0.9 immediately after mixing. LCC's also show a decline of the w/c ratio over time especially for the uncovered bars cured whilst exposed to air. Even for this curing method the critical w/c ratio is not reached after 24 hours curing.

The ULCC containing only 3% cement and the NCC with 3% Alphabond were mixed at a water/binder ratio of about 1.5. Even after 24 hours curing the w/b ratio of the ULCC and NCC is far above the critical w/c / w/b ratio. In this case the amount of water which is not needed for cement hydration is quite high, this is especially the case for the test bars cured while covered or sealed in a bag. Scrivener et al.^[5] states that water added in excess of the critical w/c = 0.35 will not be combined into the stable hydrates and will only contribute to the porosity of the paste, with an adverse effect on strength. Therefore a high amount of excess water in ULCC and NCC can have a negative impact on cured strength. The decrease of strength by moisture contained in hydraulically bonded pre-cast shapes was also discussed in previous studies for refractory materials.^[6,7]

Fig. 7 shows how the strength properties of the different curing methods relate to each other. The strength values of the test bars exposed to air drying are defined as zero and the difference in values of the other test bars are shown in percentage terms.

The strength of CC is highest when cured covered, in a plastic bag or at high relative humidity. Low strength is achieved for samples cured exposed to air drying. As the w/c ratio of 0.42 after 24 hours is below the critical limit it can be assumed that a part of the cement has not hydrated because of insufficient water availability. Strength testing after 48 hours shows no further increase and confirms this assumption.

LCC and LCC-fume achieve comparable strength levels for all curing methods. Whether part of the mixing water is able to escape or kept in the test bar with a covering, it does not impact the strength.

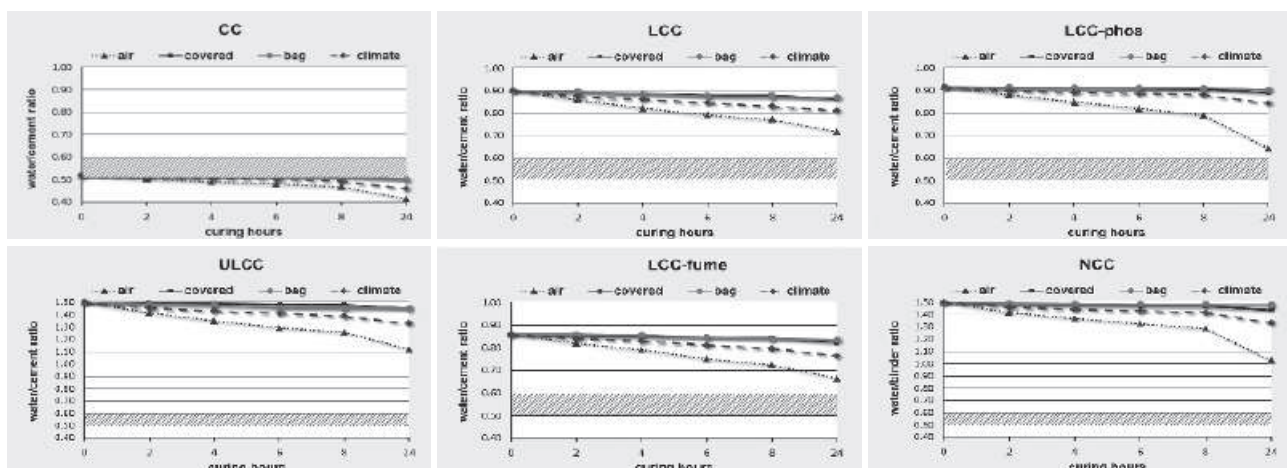


Fig. 6. Development of w/c and w/b ratio during curing up to 24 hours. The shaded area indicates the critical w/c resp. w/b ratio

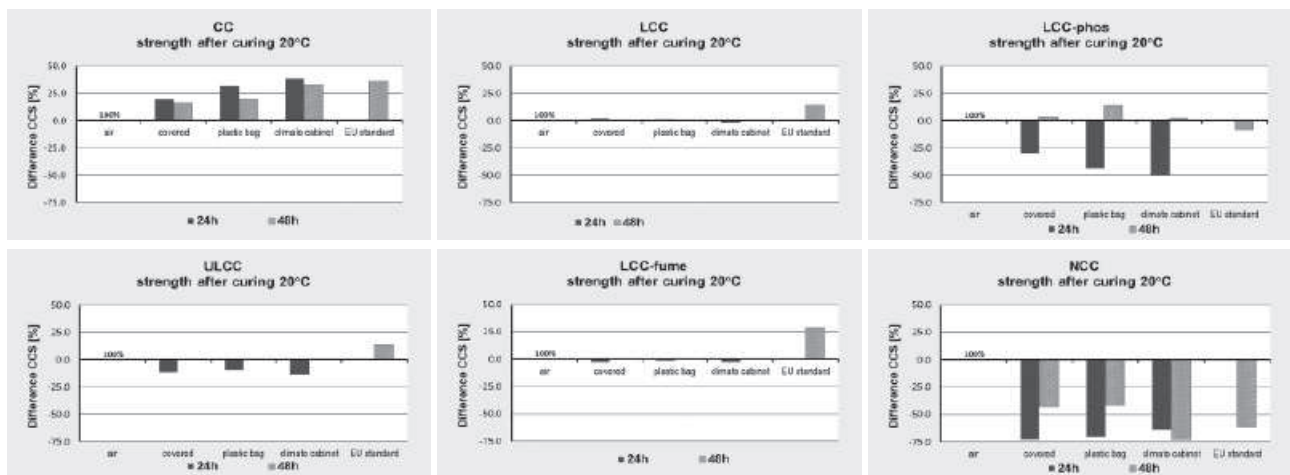


Fig. 7. Difference in cold crushing strength after 24 and 48 hours curing at 20°C by applying different curing methods

The strength properties for the LCC-phos after 24 hours look worse and are caused by a very long setting as shown in the exothermic reaction (fig. 3). The maximum temperature development occurred after more than 24h. Therefore the 48h strength values should be taken into account instead. These are then comparable to LCC and LCC-fume.

LCC's have sufficient water available for a theoretically complete cement hydration even after 24 hours curing when exposed to air drying and they do not reach the critical w/c ratio. The excess of water which is available when a covering is applied during curing is within a reasonable range and does not show a negative impact on strength.

The ULCC shows the reverse effect when compared to CC. This effect is even more pronounced with the NCC. Only a small part of the mixing water is required for the hydration of the cement or the Alfabond binder. When the excess water which is not contributing to the hydration cannot evaporate due to covering or high relative humidity, the strength of the test bar is decreased by the presence of a high amount of excess moisture as described in the literature.^[6,7]

For a proper green strength development of ULCC and NCC – type castables, it is advantageous if some of the excess water is removed from the system. Curing exposed to air can be taken as the most favorable curing method for ULCC and NCC. Practical experience with NCC pre-cast shapes, which were covered during curing, resulted in inferior performance when compared to pre-cast shapes which were cured uncovered and achieved good life. That correlates with these laboratory results.

CONCLUSION

For quality control of calcium aluminate cements, the use of test grog, where the cement is diluted by inert filler, is an essential requirement to achieve repeatable and reproducible results. The repeatability of the hydration reaction of Nortab mixture containing 80% tabular alumina and 20% cement is best when compared to neat cement testing and lower filler additions to the cement. In addition to the test method a strict control of the ambient temperature is required for the quality control of cement. Even small temperature differences from 20 to 23°C can significantly change the timing of the main cement reaction. A retarding effect has been observed for measurements of cement-bonded refractory castables performed in the climate cabinet when compared to the air-conditioned laboratory. In the climate cabinet the heat released is dissipated and is not available to heat the castable and accelerate the setting.

Calcium aluminate cements inherently develop less strength during curing at low temperatures. In addition the cured strength is impact-

ed by the curing method. For the strength development of high cement containing castables it is beneficial to cure the pieces with a covering to ensure that sufficient water is available for the cement hydration. A different curing method is recommended for ultralow and no cement castables where only a small part of the mixing water is required for the cement hydration. The removal of some of the excess water by curing the pieces whilst exposed to air improves the green strength when compared to the other curing methods. A difference between the different curing methods was not observed for low cement castable types. Well controlled ambient conditions and tailored curing conditions are key factors to achieve improved green strength properties and performance in both laboratory and application.

The curing conditions described in the standard ISO 1927-5 have in the past been developed based upon the optimum conditions for conventional, high cement containing castables. The investigation shows that ultralow and non-cement castables would require different conditions to achieve the best results. Low cement castables proved to be most robust with regard to the curing conditions and could be considered the least critical for a re-evaluation of the norm.

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