NEW CALCIUM ALUMINATE CEMENT FOR REFRACTORY PRE-CAST SHAPE PRODUCTION

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ABSTRACT

A new high alumina calcium aluminate cement (CAC) has been developed. It is called CA-SYNC. This 75% Al_2O_3 cement has a well-controlled hydration behaviour which provides advantages especially for pre-cast shape production of items such as well blocks or EAF delta sections, which incorporate inner moulds or cores. The setting shrinkage, strength development and setting behaviour were investigated in a self-flow and a vibration castable. These properties were compared to the well-known 70% Al_2O_3 cement CA-14 M. A much slower shrinkage rate was achieved with CA-SYNC. The strength development is initially slower, but continues for days resulting in higher strength levels. At dried temperatures, CA-SYNC also showed higher strength levels. After firing at temperatures of 1000°C or higher, comparable strength levels were obtained.

INTRODUCTION

The development of Calcium Aluminate Cements (CAC) started in the 19th century. They were initially developed for their chemical resistance. Later the CAC was recognised for its fast strength development and refractory properties. Towards the middle of the 20th century, high purity calcium aluminate cements were developed, and they still have an important role in the industry today. [1] These high purity CACs were used in further development of castable technologies for low moisture, self-levelling, vibration and wet gunning applications. In most applications the fast hydration of CAC is beneficial, because of strength development, but also volume shrinkage is inherent to hydration. [2] This setting shrinkage has a major impact in the production of pre-cast shapes, for example when inside moulds are applied, e.g. cones in well blocks.

A new white high alumina cement, CA-SYNC, characterised by controlled hydration, has been developed. The main reason for the development is to overcome shrinkage issues during pre-cast shape production. In the viscous stage before hydration, the volume of the castable reduces due to densification and degassing. This does not cause any stresses in the material, because the aggregates can rearrange. The shrinkage becomes critical when hydration starts and the aggregates are fixed. Preliminary research on this topic has shown that chemical shrinkage takes place within 30 minutes when common high alumina CAC is used as a binder. When the castable cannot shrink due to the presence of the inside mould, internal stresses of around 4-6 MPa will be created [3]Therefore the inside mould must not be removed too late in order to avoid cracking. In addition, enough strength has to be developed to keep the material in shape and avoid slumping. The potential of clamping of the inner moulds and related internal stresses can be determined by measuring the dimension changes of a castable during the hydration. Schleibinger Geräte developed a shrinkage measurement device based on a cone. [4-5] Shrinkage in all dimensions are reflected in the height on 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.

For successful pre-cast shape production, good workability, predictable setting time and good strength development are needed. These properties are determined by the Calcium Aluminate Cement used and can be steered by additive systems. For pre-cast shape production timing is important. Enough workability time is needed to be able to fill the moulds. With many additive systems a stiffening takes place when the material stops flowing, however, sufficient strength is not yet obtained. Sufficient strength is generated during the hydration when hydrate phases are formed. [6] Strength development is needed to be able to further process the pre-cast shape. Further processes require temperature treatment. The effect of temperature treatments on the calcium aluminate hydrates is well known. [1] The final strength will be obtained by sintering calcium aluminate phases with alumina from the fine fillers and aggregates to form calcium hexa-aluminate. High temperature resistance can be achieved when the CAC that is used has a high purity. [7]

EXPERIMENTAL PART

Sample preparation

The castables were prepared in a Hobart mixer. The solid components were added and dry mixed for one minute. After one minute the water was added and the mix wet mixed for a further four minutes. Part of the castable 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 twelve centimetres with a half cone angle of 30°. Test bars for strength measurements

Tab. 2: Castable recipes

	Self-flow	Self-flow	Vibr.	Vibr.
Tabular				
3 – 6 mm [wt%]	25	25	20	20
1 – 3 mm [wt%]	15	15	20	20
0.5 – 1 mm [wt%]	11	11	10	10
0.2–0.6 mm [wt%]	6	6	10	10
0 – 0.2 mm [wt%]	12	12	15	15
– 5 µm [wt%]	9	9		
– 0 µm [wt%]			7	7
Calcined alumina				
CTC 50 [wt%]	17	17		
CL 370 [wt%]			13	13
Cement				
CA-14 M [wt%]	5		5	
CA-SYNC [wt%]		5		5
Additives				
ADS 3 [wt%]	0.3	0.3	0.2 – 0.8	0.2 – 0.8
ADW 1 [wt%]	0.7	0.7	0.8 – 0.2	0.8 – 0.2
Water [wt%]	4.5	4.5	4.5	4.5

were cast in moulds with dimensions of 40 mm * 40 mm * 160 mm. All experiments were performed in a temperature controlled laboratory at 20°C.

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

For the self-flow castable, curing times of 3.5 – 48 hours were used. To determine the dried strength bars were cured for 6 and 24 hours, before drying at 110°C in a furnace for a further 24 hours. The standard ratio of dispersing alumina ADS 3/ADW 1 for the vibration castable was 0.2/0.8. This ratio was used to prepare the strength bars. Curing times of 2 – 72 hours were used. For temperature treated bars, standard curing was 24 hours, followed by a further 24 hours drying. Dried bars were fired for five hours at 350°C, 1000°C, 1500°C and 1650°C.

The hot modulus of rupture was measured at 1500°C for bars pre-fired at 1000°C or 1500°C for five hours.

RESULTS AND DISCUSSION

Exothermal measurements self-flow castable

In the exothermal curve, shown in Figure 1, three stages could be determined when CA-14 M was used as CAC. During mixing the temperature increased to about 25°C due to friction. In this first stage the mix is self-flowing and slowly cools. After this first stage a small increase of about 0.5°C could be observed which starts 60 minutes after mixing when CA-14 M was used. This peak is in conjunction with a stiffening behaviour of the mix. Only minimal strength is obtained at this point. 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 a strength is obtained. When CA-14 M is used this starts at 100 minutes and the maximum temperature was reached after 180 minutes. The main hydration of CA-SYNC resulted in much lower temperatures in the exothermal curve. The total temperature increase is about 1°C. The stiffening peak cannot be identified which may be caused by the overlap with the relative small hydration peak. The temperature starts to increase after 90 minutes and the peak temperature is reached after 176 minutes which is similar to CA-14 M.

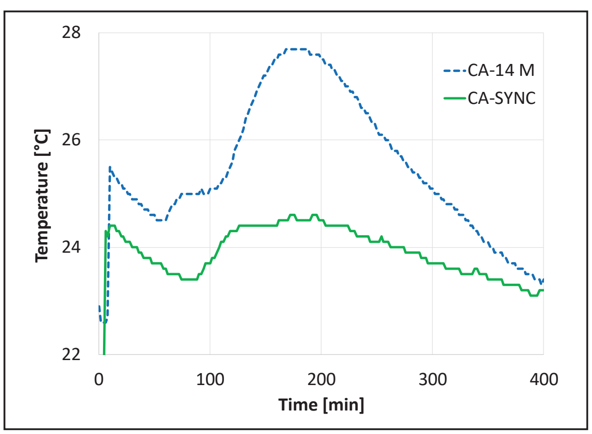

Fig. 1: Exothermal curves self-flow castable with CA-14M and CA-SYNC

Shrinkage measurements self-flow castable

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 aggregates and degassing. Because internal stresses are only created during the hydration, the shrinkage is compared from the start of the hydration. In the shrinkage curve the start of hydration can be easily determined by the increase of shrinkage rate caused by density changes. The shrinkage curves are plotted in Figure 2 and the shrinkage rate, which is the derivative of the shrinkage curves, is plotted in Figure 3. The shrinkage rate curve of CA-SYNC is flattened when compared to CA-14 M and as a result the shrinkage time of CA-SYNC in the self-flow castable is 145 minutes, while the chemical shrinkage of CA-14 M takes 40 minutes. The final shrinkage for CA-SYNC is 0.34‰ which is higher than that of CA-14 M which is 0.24‰. The final shrinkage is determined by the aggregate framework. Nevertheless the time window to remove an inside mould is increased significantly.

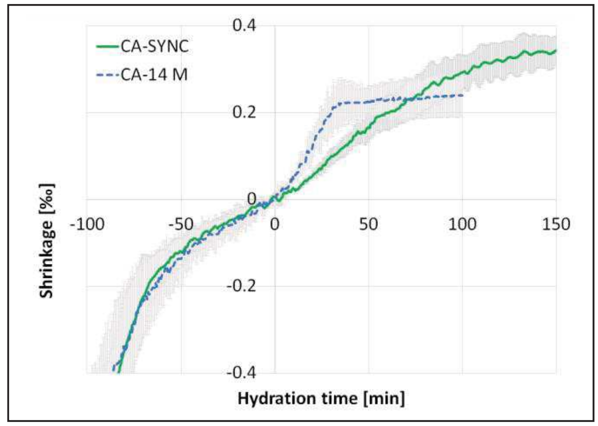

Fig. 2: Shrinkage curves self-flow castable of CA-14 M and CA-SYNC

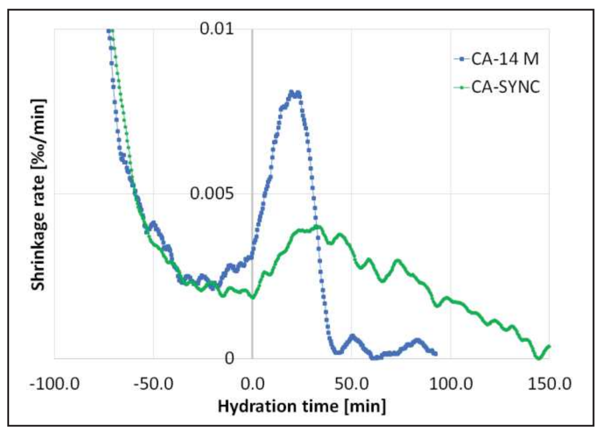

Fig. 3: Shrinkage rate self-flow castable with CA-14 M and CA-SYNC

Strength development self-flow castable

The strength levels were measured in the first hours of hydration and are plotted in Figures 4 and 5. The first strength was measured at 3.5 hours which is about 1 hour after the start of hydration. For both types of CAC a significant strength level was already generated, a cold crushing strength of 6.7 MPa for CA-SYNC and 10.7 MPa for CA-14 M. It is expected that in many cases this strength is high enough to lift and transport pieces. The strength development for CA-14 M is higher in the first hours after hydration. For CA-SYNC the strength development is slower, but continues for days, resulting in comparable 24 hour strength levels to CA-14 M and higher strength levels for bars cured for longer than 24 hours.

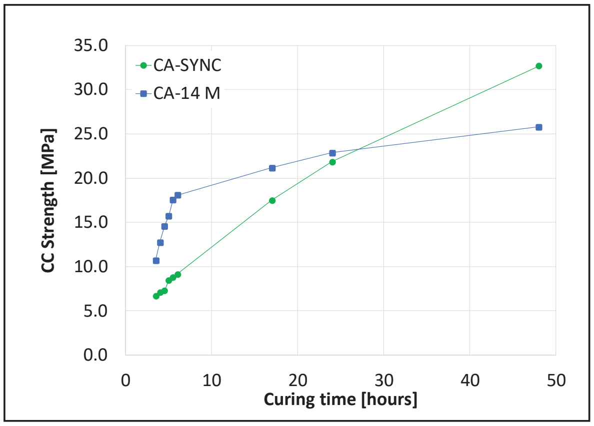

Fig. 4: Cold Crushing Strength development self-flow castable with CA-14 M and CA-SYNC

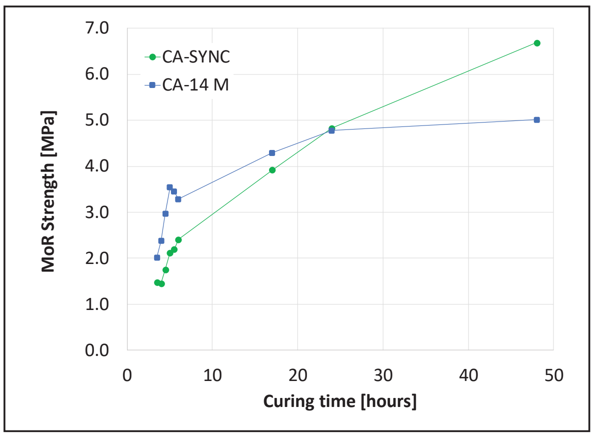

Fig. 5: Cold Modulus of Rupture strength development self-flow castable with CA-14 M and CA-SYNC

Test bars were dried after 6 hours curing time and 24 hours curing time. The strength levels of the bars are plotted in Figure 6 and 7. Although the 6 hour cured strength of CA-SYNC is lower than the strength of CA-14 M, the dried cold crushing strength of CA-SYNC is 109 MPa which is higher than the 93 MPa of CA-14 M. Longer curing times lead to even higher dried strength. For CA-SYNC a dried strength of 125 MPa was measured, while CA-14 M shows a strength of 100 MPa. Higher strength levels will be obtained when CA-SYNC is used, by longer curing times and/or by temperature treatment.

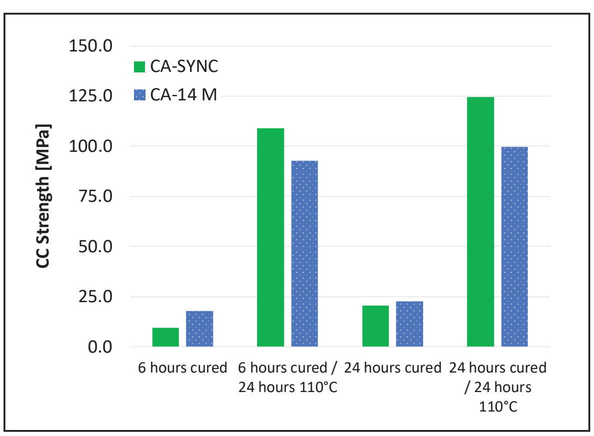

Fig. 6: Cold Crushing Strength of self-flow castable with CA-SYNC vs. CA-14 M for cured and dried test bars

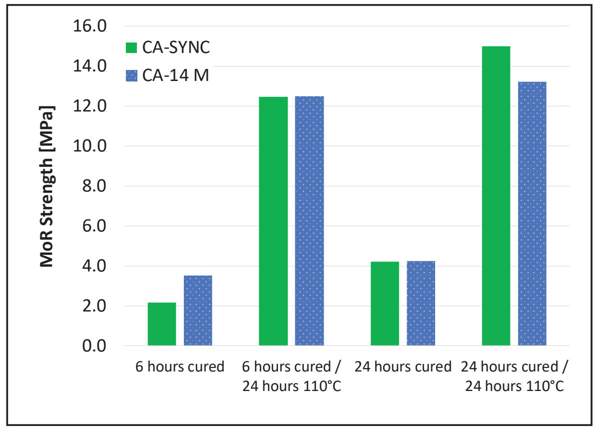

Fig. 7: Cold Modulus of Rupture for self-flow castable with CA-SYNC vs. CA-14 M for cured and dried samples

Setting time adjustment vibration castable

Different ratios of ADS/ADW were used for the vibration castable with CA-14 M as well as with CA-SYNC. The exothermal curves are shown in Figure 8. In the exothermal curves of CA-14 M a first stiffening peak can be observed and later the main hydration peak. For CA-SYNC only the main hydration peak was observed. Although the hydration peak temperatures of CA-SYNC are lower, the start and also the maximum temperatures can be controlled similar to CA-14 M. The effect of the ratio ADS 3/ADW 1 on the setting times is plotted in Figure 9. CA-SYNC could

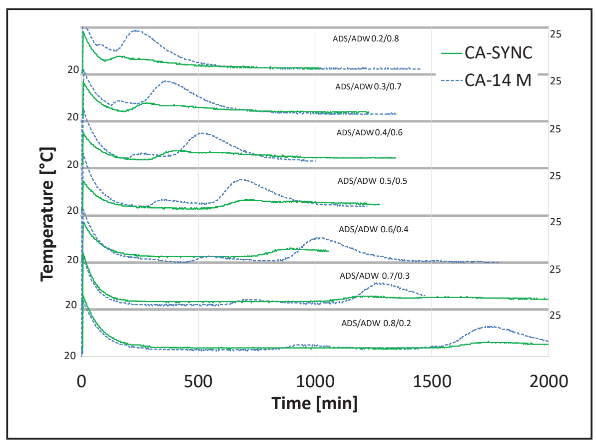

Fig. 8: Exothermal curves vibration castable with CA-14 M and CA-SYNC with different ratios ADS 3/ADW 1

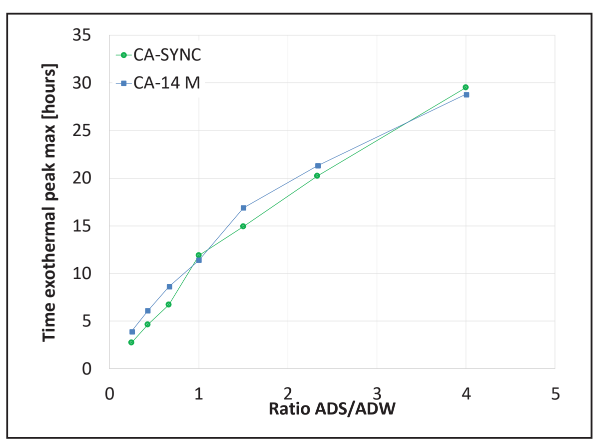

Fig. 9: Plotted time peak temperature of vibration castable with CA-14 M and CA-SYNC with different ratios ADS 3/ADW 1

be used in known recipes without changing the additive system, having the same water demand, and comparable setting times.

Strength development vibration castable

The strength development was determined for an ADS 3/ADW 1 ratio of 0.2/0.8. For CA-SYNC the hydration started at around 2.5 hours, while for CA-14 M it started at around 1.5 hours. The strength development is shown in Figure 10 and 11. The strength development for CA-SYNC started one hour later, due to the setting time. As with the self-flow castable, the strength development of CA-14 M is higher in the first hours and then slows down. It can be seen that the initial strength obtained immediately after hydration is 5 MPa cold crushing strength for CA-SYNC and also for CA-14 M. For CA-SYNC the strength development is slower when compared to CA-14, but continues for days. This strength should be sufficient for pre-cast shapes to be demoulded properly and handled for further processing. For larger pre-cast shapes such as EAF delta sections a separate removal of inner cores and the outer mould would be recommended in order to enable more strength development before handling the large pieces.

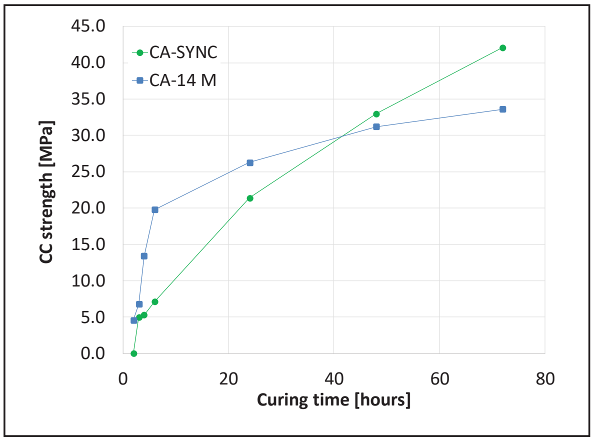

Fig. 10: Cold Crushing Strength development of vibration castable with CA-SYNC vs. CA-14 M

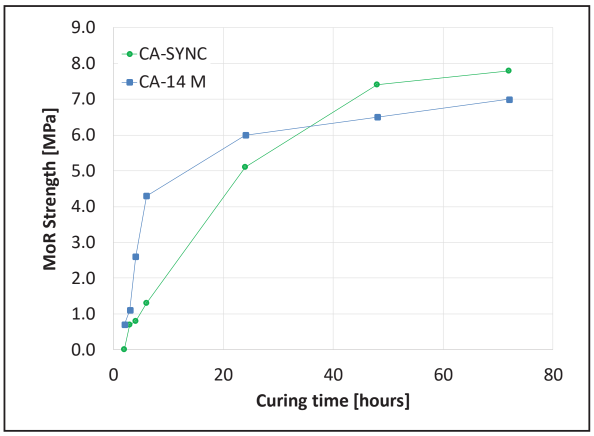

Fig. 11: Cold Modulus of Rupture development of vibration castable with CA-SYNC vs. CA-14 M

Strength during temperature treatment vibration castable

Bars were cured for 24 hours and further processed at different temperatures. The strength obtained after temperature treatment is shown in Figures 12 and 13. CA-SYNC showed higher strength levels in bars treated at intermediate temperatures (110°C and 350°C). The strength levels of bars treated at 1000°C or higher show comparable strengths for CA-SYNC and CA-14 M. This can be explained by the fact that the strength is determined by sintering of the mineralogical phases. Also the hot modulus of rupture at 1500°C for samples pre-fired at 1000°C and 1500°C, shown in Figure 14, give comparable values.

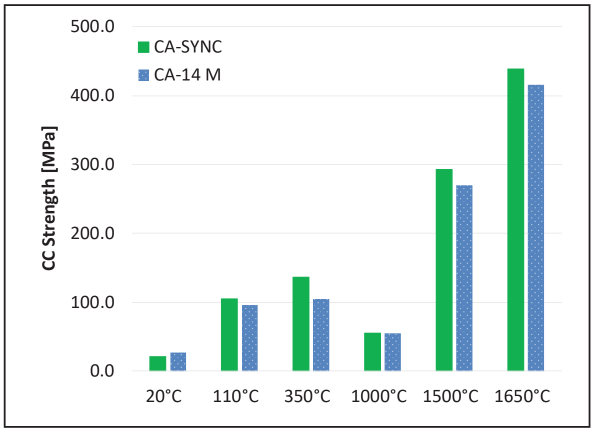

Fig. 12: Cold Crushed strength temperature treated vibration castables with CA-14 M and CA-SYNC

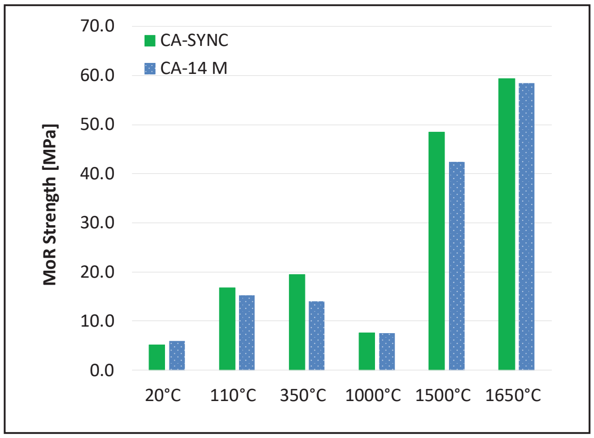

Fig. 13: Cold Modulus of Rupture of vibration castable with CA-SYNC vs. CA-14 M after different pre-firing temperatures

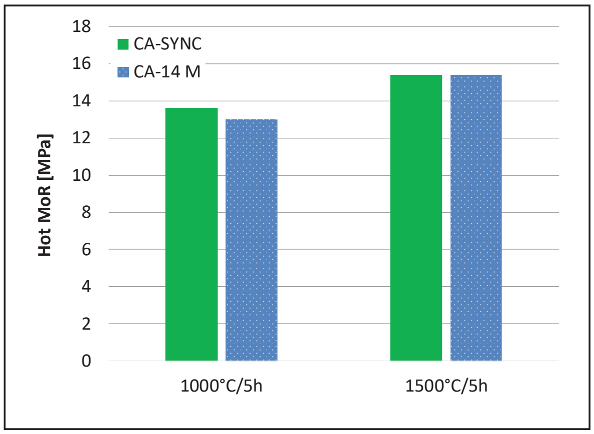

Fig. 14: Hot Modulus of Rupture at 1500°C of vibration castables with CA-SYNC vs. CA-14 M pre-fired at 1000 and 1500°C

CONCLUSIONS

The controlled hydration of CA-SYNC is reflected by a much slower setting shrinkage rate. This enables pre-cast shape producers to have a longer time window for the removal of inside moulds . The setting times of CA-SYNC can be controlled by ADS 3/ADW 1 comparable to known recipes with 70% Al_2O_3 CAC. The controlled hydration also results in higher strength levels by longer time curing and the following drying. At higher temperatures than 1000°C the strength levels are determined by sintering and are comparable to castables using CA-14 M. CA-SYNC enables pre-cast shape producers to synchronise their processes to times which suits their schedule.

The slower yet well-controlled hydration behaviour of the new CA-SYNC cement can also provide advantages in other applications other than pre-cast shape production, for example catalyst carriers, cementitious building chemistry products or additive manufacturing.

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