NEW RESULTS FOR CA-470 TI TEMPERATURE INDEPENDENT CEMENT - ROBUSTNESS AGAINST LOW TEMPERATURE AND IMPURITIES

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INTRODUCTION

The new temperature independent cement CA-470 TI is an additive free 70% Al_2O_3 cement for use in low and ultra low cement castables (LCC and ULCC). Previous investigations have shown the advantages of the new cement demonstrating a much more stable setting behaviour at different ambient temperatures between 5 and 35 °C when compared to normal 70 % Al_2O_3 cement [1,2]. When using CA-470 TI, the castables can be adjusted to a normal setting start time in the range of 1.5 to 2.5 hours at 20°C, and they will still provide a reasonable setting start time at 5 °C.

Normal 70 % alumina cements show a considerable increase of setting start at 5 °C even towards a "never setting" behaviour if the additive system is not tailored to such low ambient temperatures. An extended series of tests have been performed to further investigate the setting behaviour of CA-470 TI in low and ultra low cement castables with and without silica fume. Special focus was given on repeated testing at low temperatures and using other raw materials which are known to strongly influence the setting behaviour of castables. Eight different silica fume grades, Andalusite as aggregate, and a carbon containing castable were tested in this investigation. The strength development after curing at 5 and 20 °C was compared.

TEST CASTABLES

The composition of five different test castables is given in table 1. CA-470 TI was compared to two other 70 % Al_2O_3 cements, CA-14 M and CA-270. The dispersing alumina ratio has been adjusted to a comparable working time of 1.5 – 2.5 hours at 20 °C. In general CA-470 TI requires more retarding additives. Therefore the newly developed stronger retarding dispersing alumina M-ADS 3 was used for the silica fume containing castables with CA-470 TI. The water addition was kept constant for each test castable regardless of which cement or silica fume grade was used.

- LCC without silica fume, tabular alumina aggregate:
  Dispersing alumina ratio ADS 3 / ADW 1 was 0.8/0.2 for CA-470 TI, 0.5/0.5 for CA-14 M, and 0.4/0.6 for CA-270.
- LCC-fume, tabular alumina aggregate:
  Comparison of CA-470 TI and CA-14 M and eight different silica fume grades. 1 % dispersing alumina M-ADS 3 was used for CA-470 TI and 0.7 % M-ADS 1 + 0.3 % M-ADW 1 was used for CA-14 M. This applies for all LCC-fume test castables.
- And-LCC, Andalusite based castable with silica fume:
  Comparison of CA-470 TI and CA-14 M and two different silica fume grades. 1% dispersing alumina M-ADS 3 was used for CA-470 TI and 0.7 % M-ADS 1 + 0.3 % M-ADW 1 was used for CA-14 M.
- ULCC, tabular alumina based castable with silica fume:
  Comparison of CA-470 TI and CA-14 M and two different silica fume grades. Dispersing alumina ratio M-ADS 3 / M-ADW 1 was 0.5/0.2 for CA-470 TI and M-ADS 1 / M-ADW 1 was 0.5/0.2 for CA-14 M. ULCCs require less dispersing alumina than LCCs.
- ULCC-black, tabular alumina based castable with silica fume, SiC, and carbon:
  Comparison of CA-470 TI and CA-270, additive package was the same for both.

Tab. 1. Composition of test castables

Castable		LCC	LCC-fume	And-LCC	ULCC	ULCC-black
Tabular T60/T64						
up to 10 mm	%					15
up to 6 mm	%	70	65		65	35
Durandal up to 6 mm	%			45		
Tabular T60/T64						
- 45 MY Li	%	8	5		5	
- 20 MY	%	7	7	7	10	10
Kerphalite up to 1.6 mm	%			25		
Raw Kyanite - 100 mesh	%		5	5	5	1
SiC up to 1 mm	%					20
Silica fume	%		3	3	3	2
Reactive Alumina						
CL 370	%	10				
CTC 20	%		10	10	10	
CTC 22	%					10
70% Al_2O_3 Cement	%	5	5	5	2	3
Additives						
ADS / W	%	1				
M-ADS / W	%		1	1	0.7	
Carbon	%					3
Aluminiumpowder	%					0.3
Si powder	%					0.7
Dispersion + set control	%					0.1715
Water	%	4.9	4.5	4.5	4.5	4.5

All cements tested are high purity and have a sum of impurities (Na_2O, SiO_2, Fe_2O_3, MgO) of less than 1 %. CA-470 TI and CA-270 are finer when compared to CA-14 M (d50 7 and 6 µm vs. 13 µm). CA-470 TI is more hygroscopic when compared to other cements such as CA-14 or CA-270. It is therefore packed in sealed plastic bags to ensure a minimum shelf life of 12 months. In the laboratory the pure cement must be stored in properly closed containers to avoid aging. It is important that dry mixed castables containing CA-470 TI do not require that special packaging, but can still achieve a shelf life of one year when packed in standard bags (paper – plastic foil – paper), and when stored under adequate dry conditions. This has been tested under industrial conditions.

The reactive aluminas were CL 370 (bimodal, d50 2.5 µm, BET 3 m²/g), CTC 20 (monomodal, d50 1.8 µm, BET 2 m²/g), CTC 22 (bimodal, d50 1.9 µm, BET 2.7 m²/g). Andalusite coarse fractions were Durandal from South Africa (59.8 % Al_2O_3) and for medium to fine fractions Kerphalite from France (59 % Al_2O_3). Silicon carbide was from ESK, Germany (94 % SiC). The data of eight different silica fume grades are given in table 2. They differ in SiO_2 content. One grade contains 11 % ZrO_2. Sample 8 did not achieve a sufficient flow at 4.5 % H_2O in LCC-fume to be included in the flow comparison.

Tab. 2. Data of silica fume grades tested (information from data sheet)

Silica fume		1	2	3	4	5	6	7	8
SiO_2	%	≥ 97.5	94.5 - 97.5	95.8	85 - 88	≥ 96.0	≥ 93.0	≥ 95.5	> 90
C	%	≤ 0.8	≤ 1.4	1.3	n.s.	≤ 1.5		≤ 1.0	
ZrO_2	%				11.0				
L.O.I. @ 975°C	%	≤ 1.0		2.1		≤ 1.5	≤ 6.0	≤ 2.0	< 3.0
L.O.I. @ 750°C	%		≤ 1.8						
pH-value		4.75 - 7.5	7.0 - 8.0	6.98	2.5 - 3.5	5.0 - 8.0	5.5 - 8.0	6.5 - 8.0	

TEST CONDITIONS

The castable was dry mixed for one minute in batches of 5 kg using a Hobart A 200 planetary mixer at speed 1. The material was then stored in a closed plastic bucket at 5 °C in a climate chamber for one or three days before subsequent testing at 5 °C. Wet mixing was performed in the same mixer for 4 to 6 minutes. Some LCC-fume castables showed a longer wet out time, for example 180-200 seconds compared to the normally achieved 40-120 seconds. Therefore a longer total mixing time was needed. This can be an effect of both the silica fume grades used, and the low temperature mixing when compared to normal mixing at 20 °C.

The flow properties after 10, 30 and 60 minutes (F10, F30, F60) were measured by the cone test (lower diameter 100 mm, upper diameter 70 mm, height 80 mm). The flow comparison for LCC-fume test castables was performed at 5 °C, data for the other castables are from 20 °C testing.

The setting behaviour was tested at 5 °C in a climate chamber and the samples were stored there immediately after mixing. The setting was measured by ultrasonic equipment. The eight channel device records the velocity of ultrasound through the sample during the curing time by means of a transmitter and a receiver. The hardening of the test piece gives an increase in velocity and the initial setting coincides with the first rise in the velocity vs. curing time graph. The ultra sonic setting start has been the focus in the comparison of the test castables. For some LCC-fume castables a slight increase of velocity can sometimes be observed long before the normal steep increase occurs. This first slight increase is not correlated to the real cement hydration reaction, and these data points are therefore not considered as the start of setting.

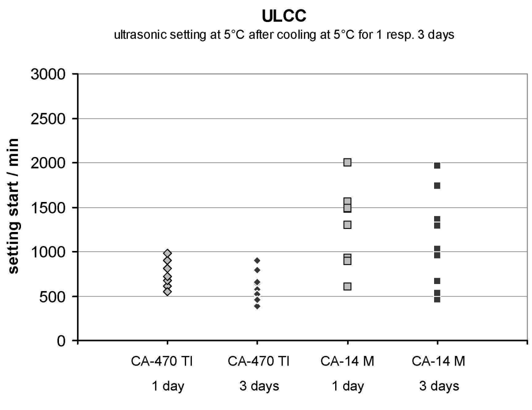
The Cold Modulus of Rupture (CMoR) was measured on 40 x 40 x 160 mm bars using the three point loading device; the Cold Crushing Strength (CCS) has been measured with the resulting halves of the CMoR bars. The focus of these tests was on the strength comparison after curing at 5 °C for 16 and 24 hours in comparison to curing at 20 °C for 24 hours.

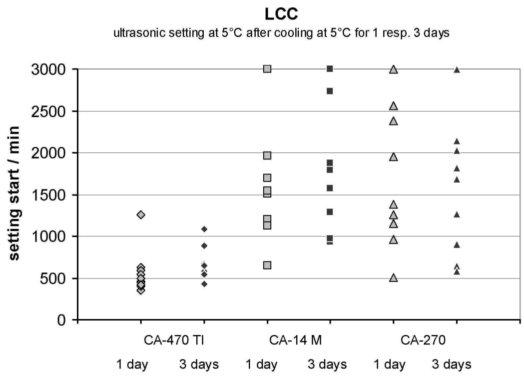
RESULTS AND DISCUSSION

Repeatability of setting at 5 °C

Previous investigations [1,2] have shown that CA-470 TI provides a much more narrow setting time range when tested at different ambient temperatures in the range from 5 to 35 °C. The advantage is shown especially at low temperatures of 5-10 °C where CA-470 TI still provides a reasonable setting start time of 7-10 hours. Normal 70 % Al_2O_3 cements show an increase of setting start of up to 20 hours or even longer at 5 °C if the additive system is not tailored to such low ambient temperatures.

Therefore further investigations were made focusing on 5 °C testing with the three test castables already used in the previous work (LCC, LCC-fume, ULCC - table 1). Identical test castables using the same raw materials and cement batches were tested up to nine times at 5 °C. The test conditions remained the same. Two test series were performed, one with samples cooled for one day at 5 °C prior to testing, the other cooled for three days. The results show a wide range of setting start time in all three test castables, from 8 to 50 hours for the normal 70 % Al_2O_3 cements even if test materials and conditions remain the same. CA-470 TI also shows some variation of setting start time but it is only between 6 and 20 hours. Normal cements may also occasionally show a reasonable setting start time at 5 °C but it can become an extended setting start far longer than 24 hours. Such behaviour is normally considered as “never setting”. In comparison, in all three test castables with and without silica fume, CA-470 TI demonstrates a setting guarantee even at low temperatures.





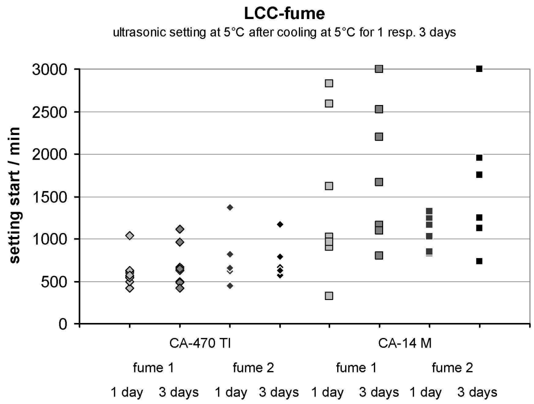
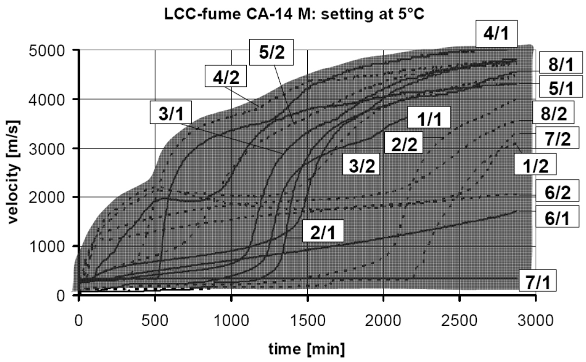


Fig. 1. Repeatability of setting start at 5 °C using ultrasonic equipment. No difference between cooling for one or three days before testing. CA-470 TI shows much more consistent behaviour in repeated testing.

Silica fume grade comparison

Each silica fume grade was tested twice in the LCC-fume at 5 °C. The setting ranges observed with the different fume grades are highlighted by a grey background in figure 2. CA-470 TI shows a much more narrow range when compared to CA-14 M and it also shows no “never setting” behaviour. The setting start time of the same fume can differ significantly between test 1 and 2 (table 3). Differences from between one and 22 hours have been observed. However, this cannot be directly attributed to the properties of the specific fume grades, for example the purity of the fume. Even the high purity fume grade 1 has shown a considerable difference in setting start time of up to 13 hours (with CA-470 TI) and even up to 40 hours (with CA-14 M) during repeated testing of LCC-fume at 5 °C (figure 1, repeated LCC-fume testing with fume grade 1 and 2).



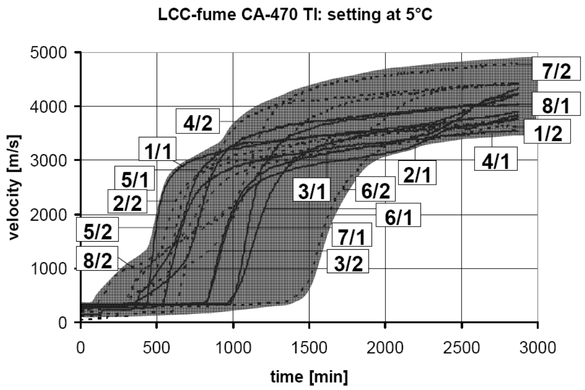


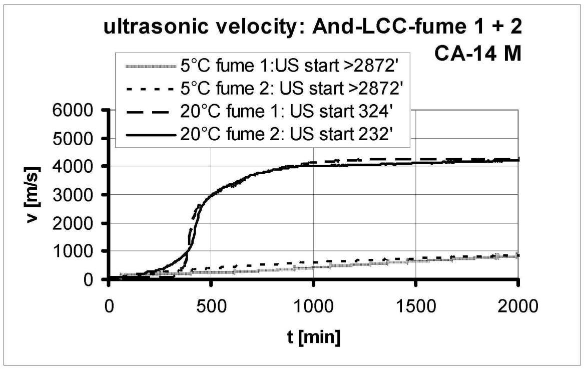
Fig. 2. Ultrasonic setting of LCC-fume with 8 different silica fume grades at 5 °C. Range of setting curves shown by grey background. CA-470 TI shows a more narrow range and no “never setting” behaviour.

Tab. 3. Ultrasonic setting start of LCC-fume at 5 °C; eight different fume grades; each test performed twice. (* slight increase in velocity not considered as the setting start).

		LCC-fume CA-470 TI	LCC-fume CA-14 M
fume 1	min	420 620	908 2200
fume 2	min	444 824	1164 1948
fume 3	min	836 (284*) / 892	1060 (20*) / 1440
fume 4	min	540 292	524 320
fume 5	min	372 536	(100*) / 852 (80*) / 732
fume 6	min	972 1396	> 2876 (28*) / > 2876
fume 7	min	988 324	> 2876 (44*) / 2604
fume 8	min	624 (68*) / 996	1352 (4*) / 2188

Andalusite LCC-fume

When Andalusite replaces Tabular alumina as the aggregate in test castable And-LCC (table 1) the ultrasonic setting start time increases at 20 °C from about 1-1.5 hours to about 3-5 hours. At 5 °C the increase of setting time is much higher and this clearly shows the advantage of CA-470 TI when compared to CA-14 M. With CA-470 TI the setting start increases from about 7 to 13 hours (fume 1) or 20 hours (fume 2), but for CA-14 M a “never setting” is observed for both fume grades (figure 3).



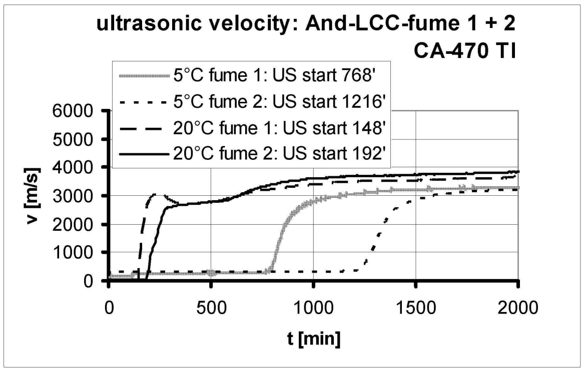


Fig. 3. Setting of Andalusite LCC with silica fume grade 1 and 2 at 5 and 20 °C. Clear advantage of CA-470 TI at 5 °C.

Strength development at 5 and 20 °C

The negative effect of low temperature curing on the strength development of refractory castables is well known. The calcium aluminate hydrates formed during hydration at low temperatures contain more water and have a lower density when compared to hydrates formed at higher curing temperatures [3-5]. The cement hydration is an exothermic reaction and the heat development supports to some extent the formation of the more desirable lower water-containing phases. This behaviour is inherent to all calcium aluminate cements.

The cold crushing strength of four different test castables after curing at 5 and 20 °C is given in figure 4. All test castables clearly show less strength after curing at 5 °C compared to 20 °C, except for ULCC after 24 hours curing. The strength after 16 hours curing at 5 °C is always lower than that obtained after 24 hours curing. CA-470 TI almost always achieves higher strength than normal 70 % Al_2O_3 cements during curing at low temperatures. This can be explained by an earlier start of setting and therefore better strength development after 16 or 24 hours. Cold modulus of rupture data are not mentioned in detail because the values after curing at 5 °C were 2 MPa or less, and the accuracy of the test equipment may be questionable at this low level. This compares to values of 4 to 8 MPa at 20 °C curing.

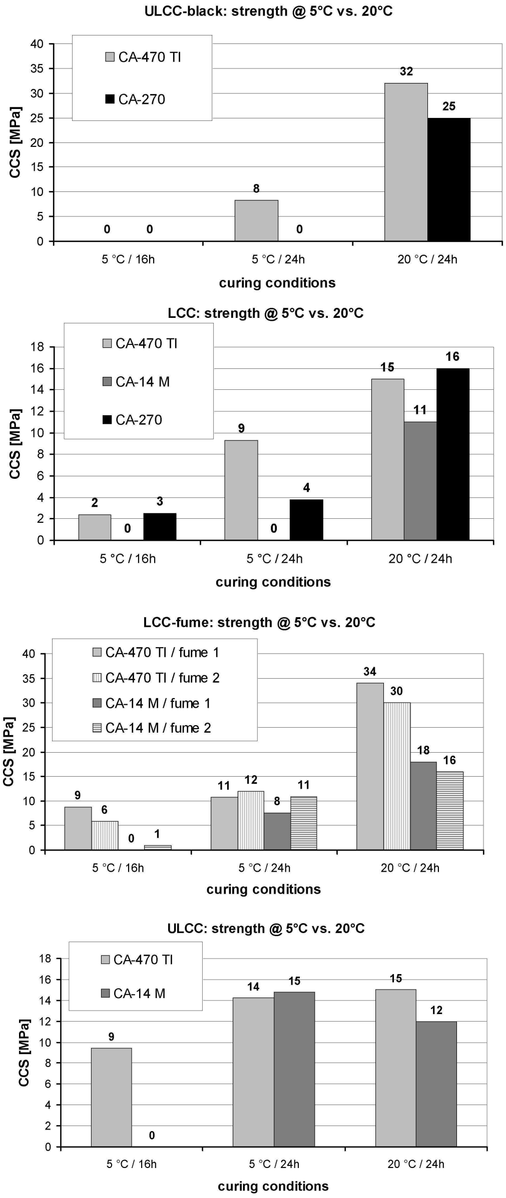


Fig. 4. Cold crushing strength of test castables after curing at 5 and 20 °C. In general lower strength at 5 °C. CA-470 TI showing advantages at low temperatures and in fume containing mixes.

Flow of silica fume containing castables

CA-470 TI has shown an improved self flowing behaviour in silica fume containing test castables, both LCC and ULCC when compared to CA-14 M [1,2]. Flow values 10 minutes after mixing were about 25 % higher in LCC and about 10 % higher in ULCC. Flow tests of And-LCC have shown the same difference: about 240 mm with CA-470 TI compared to 210 and 190 mm with CA-14 M. The lower purity fume grade 2 shows inferior flow values than fume grade 1 in the castable using CA-14 M.

Different silica fume grades can have a considerable impact on the flow behaviour of low and ultra low cement castables. Therefore the fume grades of table 2 were tested for self flowing 10 and 30 minutes after mixing. The tests were performed in LCC-fume at 5 °C in combination with the setting tests at low temperature. Fume grade 8 is the lowest purity grade and was excluded from this test because it did not achieve a self flowing behaviour at 4.5 % water addition which was taken as a standard. Fume grade 4 containing Zirconia made the castable very dilatant at 4.5 % water addition, and would require more water in a practical application.

CA-470 TI achieved a better flow behaviour than CA-14 M in all cases (figure 5): F10 is 15 to 25 % higher and F30 is 11 to 22 % higher. The fume grades 3 and 6 show a flow decay from F10 to F30 which is much worse for CA-14 M (no flow) when compared to CA-470 TI (10-25% reduced flow). The data confirm that CA-470 TI improves the flow behaviour of silica fume containing castables regardless of the purity of the fume.

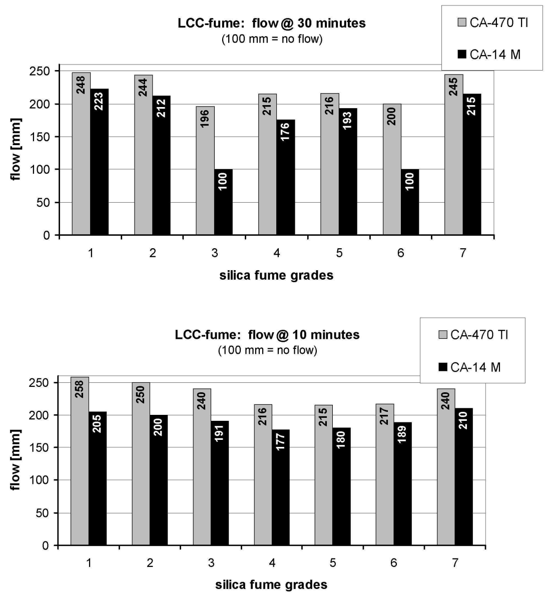


Fig. 5. Self flow data of LCC-fume with different silica fume grades. Tests performed at 5 °C. Better flow values with CA-470 TI.

In ULCC-black the flow behaviour of CA-470 TI and CA-270 were compared. Values for F10, F30, and F60 are in the range of 200 to 210 mm and show no difference between the two cement grades.

Tests with Almatis Integrated Matrix products

Almatis Integrated Matrix (AIM) products are an integrated matrix of aggregate fines, calcined, reactive and dispersing aluminas, for use in tabular alumina, spinel or other high alumina aggregate refractory castables. 70 % Al_2O_3 cement is all that must be added to complete the refractory matrix [6]. Dispersing alumina in AIM products has been adjusted for use with normal 70 % Al_2O_3 cements (CA-14 W, M, or S and CA-270). Tests at 20 °C with all AIM products and CA-470 TI in low and ultra low cement castables have shown that the new cement can also be used for these products, but the working time is shorter. The start of setting occurs after about 1 hour when compared to a normal 2-3 hours and the exothermic maximum occurs after 3-5 hours instead of 6-8 hours.

CONCLUSION

The new temperature independent cement CA-470 TI shows clear advantages when compared to standard 70 % Al_2O_3 cements:

- Better flow behaviour in silica fume containing castables when compared to CA-14,
- Robust setting behaviour even with criticial raw materials (various silica fume grades, Andalusite aggregate),
- Setting guarantee.

CA-470 TI improves the setting behaviour of castables at low temperature whether or not they contain silica fume. Castables with CA-470 TI exhibit a much more robust setting and avoid the setting time variability and uncertainty which are especially apparent during winter time. Repeated testing at 5 °C has shown that normal 70 % Al_2O_3 cements may give a reasonable setting time occasionally but it can also become “never setting”. CA-470 TI avoids this “never setting” in all test castables and thereby provides a setting guarantee.

The flow of silica fume containing mixes is improved by 10-25 % when using CA-470 TI instead of normal 70 % Al_2O_3 cement CA-14 M. Tests with different silica fume grades and Andalusite as aggregate have confirmed the robustness of CA-470 TI exhibiting reliable setting behaviour even at low ambient temperature.

Calcium aluminate cements inherently develop less strength during curing at low ambient temperatures. In general the new cement cannot overcome this problem, but it does ensure the setting of the castable and improves the strength development when compared to normal 70 % Al_2O_3 cement.

First industrial trials with CA-470 TI are ongoing. The improved flow behaviour and robust setting characteristics have been proven in these trials.

REFERENCES

[1] Buhr A, Gierisch D, Groß HL, Kraaijenbos FW, Wams G, Dutton J. A new temperature independent cement for low and ultra low cement castables. Proceedings of UNITECR´07, 2007 Sep 18-21, Dresden, Germany, 396-400.

[2] Buhr A, Gierisch D, Groß HL, Kraaijenbos FW, Wams G, Dutton J. Comparison of a new temperature independent cement with other 70 % Al2O3 cements for low and ultra low cement refractory castables. Proceedings of the Centenary Calcium Aluminate Cement conference, 2008 Jun 30 – Jul 2, Avignon, France, 405-416.

[3] Givan GV, Hart LD, Heilich RP, MacZura G. Curing and firing high purity calcium aluminate-bonded tabular alumina castables. Ceramic bulletin, Vol 54, No 8, 1975, 710-713.

[4] Roesel RE, MacZura G, Rothenbuehler PT. Calcium aluminate cements for high strength refractory monolithics. Interceram 31, No 5, 1982, 519-523.

[5] Kopanda JE, MacZura G. Production processes, properties, and applications for calcium aluminate cements. Alumina Science and Technology Handbook, ed. By LeRoy D. Hart, American Ceramic Society, 1990, 171-183.

[6] Refractory Matrix Brochure. Almatis GP-RCP/012/R07/0608, available under www.almatis.com.