A NEW TEMPERATURE INDEPENDENT CEMENT FOR LOW AND ULTRA LOW CEMENT CASTABLES

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INTRODUCTION

Low and ultra low cement castables (LCC and ULCC) are widely used for in-situ installations and for the manufacturing of pre-cast shapes. High alumina calcium aluminate cements are a key component of these formulations, although they are only added in small amounts. The workability of the mixes with regard to water demand, pot life, setting time, strength development is strongly influenced by the cement used in the formulation. The chemical purity of the cement also has a major impact on the hot properties of the castable. For the formulation of low and ultra low cement castables, additive free 70% alumina cements with a very low amount of impurities are normally used.

High quality cements must show high consistency in their product properties. This is important for the user to achieve the desired and predictable behaviour of the final mix. Of course, other important components of low and ultra low cement castables also have a major impact on the behaviour of the mixes. These include fine fillers like calcined and reactive aluminas, silica fume, fine aggregates, and additives for dispersion of the fines and for steering the setting behaviour of the mix.

When using appropriate components in the formulation of the mix, it is possible to adjust the pot life and setting times of low and ultra low cement castables according to the requirements of the final application. The setting time requirements can be very different. For on-site installations longer setting times are usually required compared to the times required for in-house production of pre-cast shapes.

When using consistent high quality cement and additives such as dispersing aluminas, the setting behaviour of castables can also be tailored to different temperature conditions. However, for a given mix composition, which has been adjusted for a specific temperature range, the setting time can change significantly if the ambient temperature is outside the expected range. For example, the start of setting of a low cement castable, which has been adjusted to 200 minutes at 20°C, can increase to over 1000 minutes at 5°C. This inherent temperature dependency of the hydration reaction of the cement is a well known source of problems. This is especially applicable for on-site installations during seasonal changes or for export business into regions with different climatic conditions.

NEW CEMENT CA-470 TI

The new, additive free 70% alumina cement CA-470 TI has been developed. This significantly reduces the setting time variations at different temperatures. It is intended specifically for castables with low or ultra low cement content using dispersing systems, without or with silica fume. Typical data are given in table 1.

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 6 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 achieve a shelf life of one year when packed in standard bags (paper – plastic foil – paper), and if stored under adequate dry conditions.

TEST CASTABLES

Data of the cements used are given in table 1. Tabular alumina T60/T64 was the aggregate used. The matrix contains Tabular alumina fines (-45MY(-325) LI and -20MY), reactive aluminas CL 370 (bimodal, d50 2.6µm, BET 3m²/g) resp. CTC 20 (monomodal, d50 1.9µm, BET 2m²/g). The silica fume containing castables also contain 5% of raw Kyanite to overcome firing shrinkage at temperatures above 1350°C. The purity of silica fume has an influence on the workability and setting time of the castable. Therefore two different grades of silica fume (table 2) were tested in the low cement castable.

In general CA-470 TI requires more retarding additives, therefore a new stronger retarding dispersing alumina M-ADS 3 for silica fume

containing castables has been developed and introduced.
CA-470 TI has been compared to CA-14 M and CA-270 in three different test castables:

- LCC without silica fume (table 3)
- LCC with silica fume (table 4)
- ULCC with silica fume (only vs. CA-14 M, and only Elkem 971 U silica fume, table 5)

The setting time of the castables at 20°C has been adjusted to a comparable working time and EXO max range by varying the additions of dispersing aluminas.

Tab. 1. Typical data of cements

Chemical Analysis		CA-470 TI	CA-14 M	CA-270
Al_2O_3	%	72	71	72
CaO	%	27	28	27
Na_2O	%	0,2	0,2	0,2
SiO_2	%	0,2	0,2	0,2
Fe_2O_3	%	0,1	0,1	0,1
MgO	%	0,2	0,2	0,2
Physical Properties				
- 45 µm	%	90	82	88
Cilas D50	µm	7	13	6

Tab. 2. Data of silica fume (data sheets from Internet May 2007)

	Elkem Micro-silica "971-U"	RW silicium GmbH "RW-Füller"	
		typical	
SiO_2 [%]	min. 97,5	(diff.) 96,0	± 1,5
C [%]	max. 0,8	not specified	
C_{free} [%]	not specified	0,6	max. 1,4
SiC [%]	not specified	0,6	max. 0,9
Fe_2O_3 [%]	max. 0,3	0,05	max. 0,15
Al_2O_3 [%]	max. 0,7	0,2	max. 0,5
CaO [%]	max. 0,3	0,25	max. 0,35
MgO [%]	max. 0,5	0,4	max. 0,6
K_2O [%]	max. 0,6	1,2	max. 1,8
Na_2O [%]	max. 0,3	0,1	max. 0,2
L.O.I. [%]	max.1,0 (at 975°C)	1,2 (< 750°C)	max. 1,8
> 45 µm [%]	max. 0,6	ca. 1,5	
pH	4,5 - 7,5	7,5	± 0,5

Tab. 3. Low cement test castables without silica fume

Castable		LCC	LCC	LCC
		CA-470 TI	CA-14 M	CA-270
Tabular T60/T64 Up to 6 mm	%	70	70	70
T60/T64 -45 MY Li	%	8	8	8
T60/T64 -20 MY	%	7	7	7
Reactive Alumina CL 370	%	10	10	10
Cement				
CA-470 TI	%	5		
CA-14 M	%		5	
CA-270	%			5
Additives				
ADS 3	%	0,8	0,5	0,4
ADW 1	%	0,2	0,5	0,6
Water	%	**4,9**	**4,9**	**4,9**
Wet out time	sec	60	70	60
Self flow				
10 min	mm	250	254	262
30 min	mm	263	261	270
60 min	mm	268	250	250
EXO				
Start 1		158' / 23,6°C	197' / 23,3°C	304' / 25,6°C
Start 2		5,5h / 26,6°C	6,0h / 25,2°C	6,3h / 27,3°C
Max		7,1h / 33,5°C	8,5h / 29,5°C	8,1h / 34,7°C
Ultrasonic setting start	min	144	136	352
CMoR				
20°C / 24h	MPa	5	3	5
110°C / 24h	MPa	15	12	18
1000°C / 5h	MPa	12	10	10
1500°C / 5h	MPa	47	46	38
CCS				
20°C / 24h	MPa	15	11	16
110°C / 24h	MPa	66	66	73
1000°C / 5h	MPa	67	44	59
1500°C / 5h	MPa	130	82	107
Density				
110°C / 24h	g/cm³	3,14	3,13	3,14
1000°C / 5h	g/cm³	3,08	3,04	3,08
1500°C / 5h	g/cm³	3,10	3,11	3,02
Shrinkage				
110°C / 24h	%	-0,04	-0,02	-0,03
1000°C / 5h	%	-0,01	+0,06	+0,09
1500°C / 5h	%	-0,03	-0,09	+0,18
HMoR				
1500°C / 5h	MPa	18	18	18

Tab. 4. Low cement test castables with silica fume

Component \ Castable			LCC-fume 1	LCC-fume 2	LCC-fume 1	LCC-fume 2
			CA-470 TI	CA-470 TI	CA-14 M	CA-14 M
Coarse fraction	Tabular T60/T64	%	65	65	65	65
	up to 6 mm					
Fine fraction	T60/T64 -45 MY Li	%	5	5	5	5
	T60/T64 -20 MY	%	7	7	7	7
Raw Kyanite	-100 mesh	%	5	5	5	5
Reactive Alumina	CTC 20	%	10	10	10	10
Silica fume	Elkem 971U	%	3		3	
	RW Füller			3		3
Cement	CA-470 TI	%	5	5		
	CA-14 M	%			5	5
Additives	M-ADS 1	%			0,7	0,7
	M-ADS 3	%	1	1		
	M-ADW 1	%			0,3	0,3
Water		%	**4,5**	**4,5**	**4,5**	**4,5**
wet out time		sec	60	80	40	60
self flow	10 min	mm	258	250	205	200
	30 min	mm	248	244	223	212
	60 min	mm	184	189	202	221
EXO	Start 1		77' / 24,6°C	94' / 23,8°C	65' / 24,3°C	124' / 23,0°C
	Start 2		4,2h / 27,1°C	3,8h / 24,8°C	3,4h / 26,3°C	4,6h / 25,3°C
	Max		5,8h / 30,8°C	5,8h / 28,7°C	5,4h / 28,8°C	6,6h / 28,0°C
ultrasonic setting start		min	84	92	64	72
CMoR	20°C / 24h	MPa	7	8	5	5
	110°C / 24h	MPa	20	19	21	19
	1000°C / 5h	MPa	22	24	25	28
	1400°C / 5h	MPa	44	44	48	56
CCS	20°C / 24h	MPa	34	30	18	16
	110°C / 24h	MPa	96	105	100	97
	1000°C / 5h	MPa	170	136	166	173
	1400°C / 5h	MPa	210	232	233	195
Density	110°C / 24h	g/cm³	3,06	3,05	3,03	3,05
	1000°C / 5h	g/cm³	3,04	3,00	3,01	3,00
	1400°C / 5h	g/cm³	3,03	3,06	2,97	3,02
Shrinkage	110°C / 24h	%	+0,04	-0,03	-0,04	-0,06
	1000°C / 5h	%	+0,12	-0,09	-0,11	-0,07
	1400°C / 5h	%	-0,11	-0,27	-0,02	-0,31

Tab. 5. Ultra low cement test castables with silica fume

Castable		ULCC CA-470 TI	ULCC CA-14 M
Tabular T60/T64 up to 6 mm	%	65	65
T60/T64 -45 MY Li	%	5	5
T60/T64 -20 MY	%	10	10
Raw Kyanite -100 mesh	%	5	5
Reactive Alumina CTC 20	%	10	10
Silica fume Elkem 971U	%	3	3
Cement			
CA-470 TI	%	2	
CA-14 M	%		2
Addtitives			
M-ADS 1	%		0,5
M-ADS 3	%	0,5	
M-ADW 1	%	0,2	0,2
Water	%	**4,5**	**4,5**
wet out time	sec	45	40
self flow			
10 min	mm	255	238
30 min	mm	264	235
60 min	mm	250	180
Ultrasonic setting start	min	92	76
CMoR			
20°C / 24h	MPa	4	3
110°C / 24h	MPa	7	6
1000°C / 5h	MPa	42	49
1500°C / 5h	MPa	44	44
CCS			
20°C / 24h	MPa	15	12
110°C / 24h	MPa	63	55
1000°C / 5h	MPa	179	200
1500°C / 5h	MPa	165	228
Density			
110°C / 24h	g/cm³	3,08	3,14
1000°C / 5h	g/cm³	3,07	3,04
1500°C / 5h	g/cm³	3,11	3,08
Shrinkage			
110°C / 24h	%	-0,02	-0,01
1000°C / 5h	%	-0,07	-0,05
1500°C / 5h	%	-0,40	-0,57

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 and then wet mixed for 4 minutes. The castables were tested at a constant water addition as stated in tables 3-5. The wet out time was determined as described in a previous paper [1]. The flow properties after 10, 30, and 60 minutes were measured by the cone test (lower diameter 100 mm, upper diameter 70 mm, height 80 mm).

The setting behaviour was determined by exothermic measurement (only at 20°C) and by the use of ultrasonic test equipment [2]. Both methods show good correlation (figure 1), but the ultrasonic test is more sensitive especially for ultra low cement castables.

The setting behaviour was tested at 5, 10, 20 and 35 °C in a climate chamber. The dry mixed castable was stored for 24 hours at the test temperature in the climate chamber. The samples for setting test measurement were also stored in the climate chamber immediately after wet mixing.

The flow at 30 and 60 minutes, and strength and firing data were only measured for the samples, which set at room temperature.

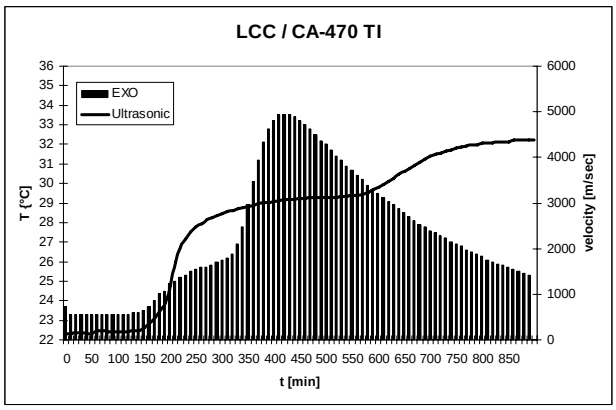


Fig. 1. Measurement of LCC CA-470 TI setting by exothermic reaction and ultrasonic equipment

RESULTS AND DISCUSSION

LCC without silica fume

LCC CA-470 TI clearly shows much less variance in setting times at different temperatures when compared to LCC CA-14 M and LCC CA-270 (table 6 and figure 2). LCC CA-470 TI shows a clear advantage at 10°C and even greater advantage at 5°C ambient temperature. The start of setting increases only to 3.5 and 11 hours at these low temperatures. For LCC CA-14 M and LCC CA-270 the start of setting increases significantly more, up to 19 to 25

hours, and even up to 40 hours for LCC CA-270 at 5°C. Here, the castables could not be relied upon to set overnight during on-site installations. This can become a big problem in industrial applications, if the mould is removed too early. CA-470 TI can overcome this problem.

Water demand, wet out time and flow behaviour up to 60 minutes are practically the same for the three test castables (table 3). LCC CA-470 TI requires a higher ratio of retarding dispersing alumina ADS 3 when compared to LCC CA-14 M and LCC CA-270 to achieve a comparable setting time at 20°C. LCC CA-270 shows a later start of setting at 20°C (300-350 minutes) but a comparable EXO max of around 8 hours. The hot modulus of rupture at 1500°C is 18 MPa for all castables.

Tab. 6. LCC test results at 5 to 35°C.

Castable Cement		LCC CA-470 TI	LCC CA-14 M	LCC CA-270
wet out time				
5°C	s	60	60	45
10°C	s	60	60	45
20°C	s	60	70	60
35°C	s	60	60	45
self flow at 10 min				
5°C	mm	260	250	265
10°C	mm	265	260	260
20°C	mm	250	254	262
35°C	mm	287	278	274
ultrasonic setting start				
5°C	min	656	1504	2380
10°C	min	336	1396	1116
20°C	min	144	136	352
35°C	min	56	60	108
Difference 5 - 35°C	**min**	**600**	**1444**	**2272**

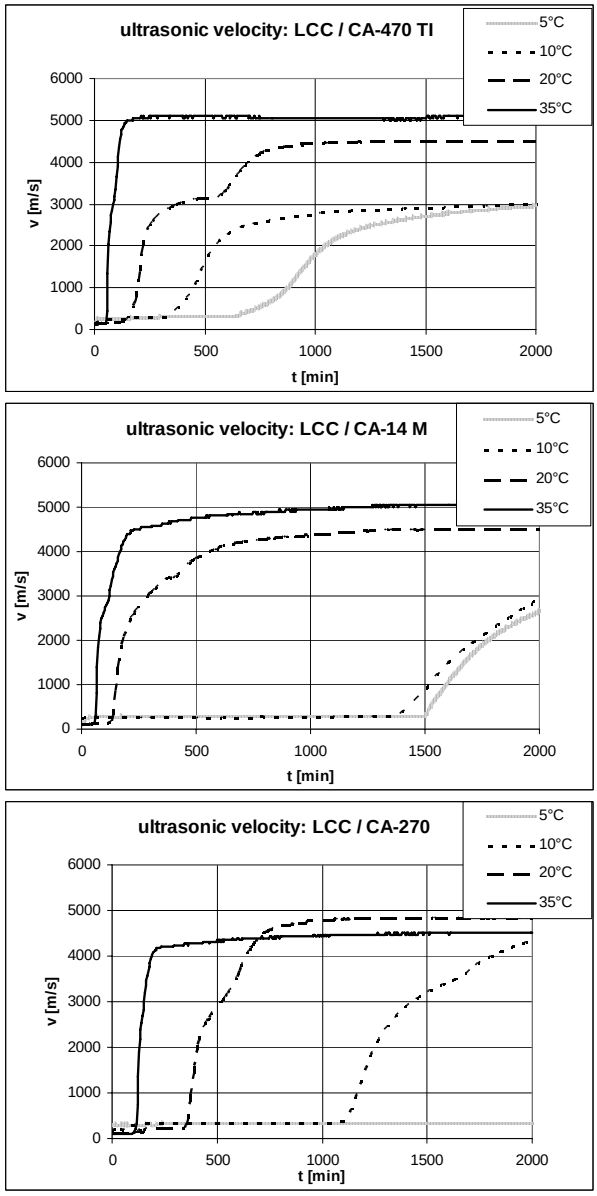


Fig. 2. Setting of LCC test castables. Clear advantage of CA-470 TI at 5 and 10°C. Setting start LCC CA-270 at 5°C at 2380 minutes.

LCC with silica fume

CA-470 TI also significantly reduces the variation in setting time for the silica fume containing castable (table 7 and figure 3). Here the setting times at 10 to 35 °C are comparable, but at 5 °C LCC FUME CA-470 TI shows a clear advantage. With both fume grades, LCC FUME CA-470 TI starts to set after about 7 hours whereas the start of setting of LCC FUME CA-14 M increases to 15 hours with Elkem 971 U and 19 hours with RW Füller.

Both test castables show a trend towards longer setting for the less pure RW Füller. The LCC containing silica fume with CA-470 TI requires a stronger retarding additive (1 % M-ADS 3) when compared to LCC FUME CA-14 M (table 4).

Mixing time to achieve wet out is lower for LCC FUME CA-14 M when compared to CA-470 TI. Both test castables require longer mixing time to achieve wet out for the silica fume grade with lower SiO_2 content (RW Füller). This also confirms the general experience with other test castables. The flow at 10 minutes is about 25% higher with CA-470 TI when compared to CA-14 M (table 7).

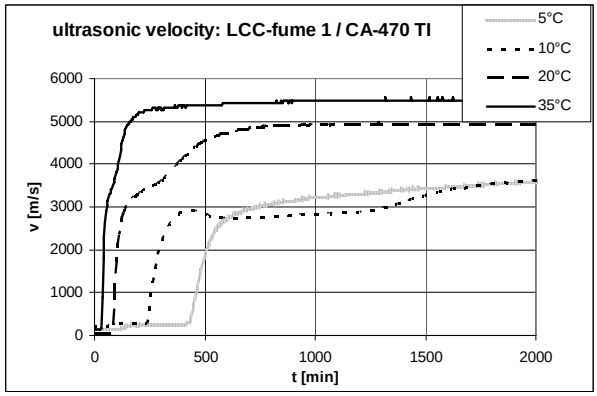
The green strength after 24 hours at 20°C is about 50% higher with CA-470 TI.

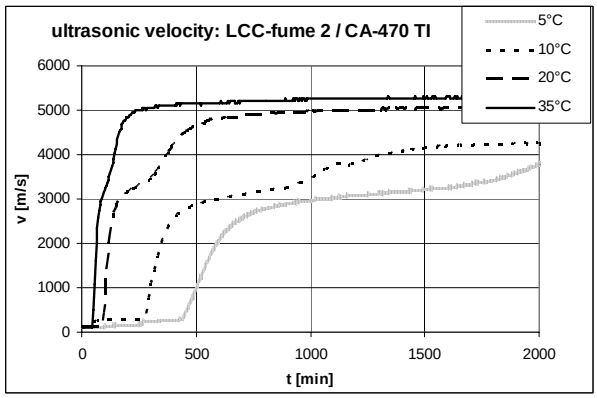
Tab. 7. LCC with silica fume test results at 5 to 35°C.

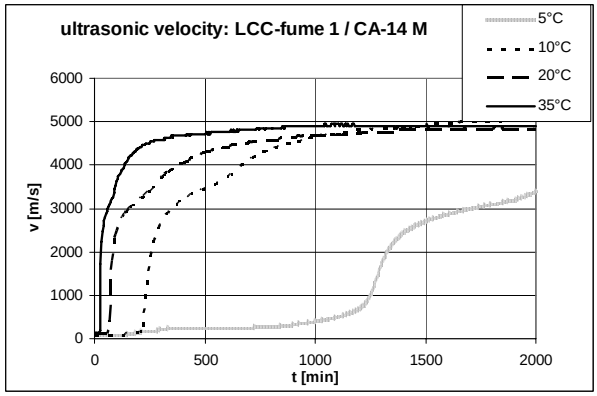
Castable Cement		LCC-fume 1 CA-470 TI	LCC-fume 2 CA-470 TI	LCC-fume 1 CA-14 M	LCC-fume 2 CA-14 M
wet out time					
5°C	s	90	120	60	60
10°C	s	90	75	70	70
20°C	s	60	80	40	60
35°C	s	80	80	60	70
self flow at 10 min					
5°C	mm	248	226	212	182
10°C	mm	245	259	195	188
20°C	mm	258	250	205	200
35°C	mm	230	248	201	196
ultrasonic setting start					
5°C	min	420	444	908	1164
10°C	min	244	272	224	276
20°C	min	84	92	64	72
35°C	min	36	52	24	52
difference 5 - 35°C	**min**	**384**	**392**	**884**	**1112**

Tab. 8. ULCC with silica fume test results at 5 to 35°C.

Castable Cement		ULCC CA-470 TI	ULCC CA-14 M
wet out time			
5°C	s	50	50
10°C	s	55	50
20°C	s	45	40
35°C	s	60	40
self flow at 10 min			
5°C	mm	250	240
10°C	mm	247	236
20°C	mm	255	238
35°C	mm	246	235
ultrasonic setting start			
5°C	min	616	1480
10°C	min	216	384
20°C	min	92	76
35°C	min	24	36
difference 5 - 35°C	**min**	**592**	**1444**







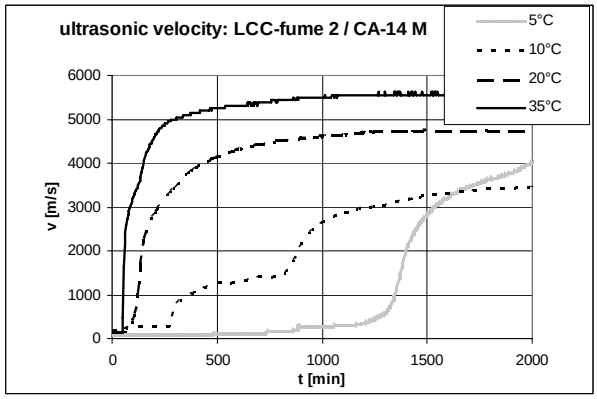


Fig. 3. Setting of LCC with silica fume test castables. Clear advantage of CA-470 TI at 5°C.

ULCC with silica fume

ULCC CA-470 TI shows a better flow when compared to ULCC CA-14 M (table 5 and 8). At 5°C ULCC CA-470 TI gives a much shorter setting time of 10 hours in comparison to ULCC CA-14 M (25 hours, figure 4). Also at 10°C the setting start is shorter with CA-470 TI (3.6 vs. 6 hours). In spite of the low cement content of only 2% in the formulation, the setting at low temperature becomes much more robust with CA-470 TI.

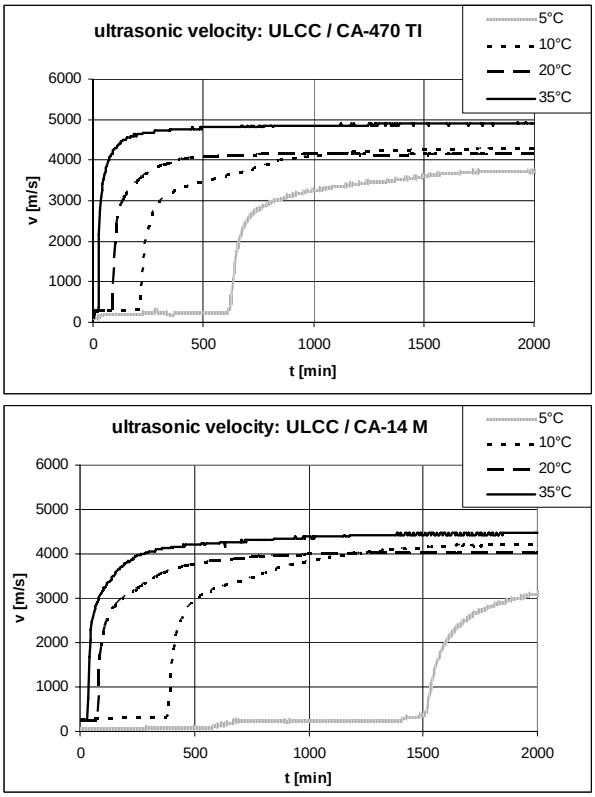


Fig. 4. Setting of ULCC with silica fume test castables. Clear advantage of CA-470 TI at 5°C.

CONCLUSION AND OUTLOOK

The new temperature independent cement CA-470 TI shows a clear advantage in the setting behaviour of all test castables at low temperature whether with or without silica fume. 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 of 7 to 10 hours at 5°C. Normal 70 % alumina cements show an increase of setting start to 20 hours and even more at 5°C if the additive system is not tailored to such low ambient temperatures. Castables with CA-470 TI will exhibit a much more robust setting behaviour and will avoid the setting time variability and uncertainty which are especially apparent during winter time.

Risky countermeasures of adding tiny amounts of accelerating additives during on site installations can be avoided.

No tests have been made yet using CA-470 TI with other aggregates such as Andalusite, which could also contribute to a retarded setting of low cement castables. The stable results with CA-470 TI and different silica fume grades in the LCC FUME indicate a more robust behaviour of CA-470 TI against impurities from other castable compounds. This will be investigated by a further series of tests in the future.

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