

Re-engineered Calcium Aluminate Cement for Refractory Castables

M. Schmid, R. Kaden, G. Walenta

The effect of Calcium Aluminate Cement (CAC) fineness and mineralogy on workability and high temperature performance of two commercial available CAC was investigated. A medium CAC with low $C_{12}A_7$ content and a high specific surface area leads to improved flow and higher strength after firing a regular cement castable with fireclay. A higher specific surface of the CAC enhances sintering of the calcium aluminates with the fireclay aggregates. Improved refractory castable properties of the fine ground CAC can be attributed to a higher crystalline phase content and increased hibonite formation at high temperatures.

1 Introduction

Calcium Aluminate Cements (CAC) are the most applied hydraulic binders in refractory castables because they ensure fast setting, high strength and resistance to a wide range of aggressive environments. Since their first invention at the beginning of the 20th century, a big step in their evolution has been made. Nowadays, they are ranging from iron rich, low alumina CAC up to high purity high alumina cements [1, 2]. CAC chemistry and mineralogy has been widely studied and is still a field of ongoing research. The optimisation of refractory binders is an ongoing process and led to performance-optimised products like magnesium calcium aluminate cement [1] and high-performance CAC with a CA content higher than 90 mass-% [4]. Especially, the determination of phase composition with Rietveld method [5] has become now state of the art in CAC cement production and enables high product quality and performance.

CA, mono-calciumaluminate ($CaAl_2O_4$) is – amongst the hydraulic calcium aluminate phases – the major component in most common available CACs and responsible for hardening and strength development. $C_{12}A_7$ might deliberately be present or absent in

medium- and low-alumina cements and is a fast setting in CAC.

Beside optimised mineralogy, latest research focuses on optimisation of hydration behaviour and how to increase the degree of hydration of CA [6]. Zhang et al. [7, 8] focused on commercial available CAC and additional lab grindings. By examination of different fine ground CAC, it was found that a higher fineness leads to increased open time and higher strength after firing at 110 °C and 800 °C. But this investigation was done with a CAC containing ca. 70 mass-% alumina and exclusively the phases CA and CA_2 .

The authors focus their investigation on 2 medium-alumina cements with approximately 50 mass-% Al_2O_3 according to Lea [2]. The 1st one is an already commercial available product which has been sold for more than 20 years to the refractory industry. The 2nd CAC is a re-engineered CAC of similar chemical composition but optimised and controlled low $C_{12}A_7$ and with a specific surface area of 4380 cm²/g. Both cements were tested according to EN 14647 and compared on basis of setting and strength development at room temperature. Performance comparison of both CAC in a regular castable with fireclay aggregates demonstrate the difference in

workability, setting and hardening behaviour of the 2 tested CACs. High-temperature application tests and quantitative phase analysis provides an insight into the interactions about the cements with aggregates up to 1400 °C.

2 Raw materials and experimental procedure

CAC 50, CAC 505 and fireclay chemical compositions are listed in Tab. 1.

CAC 50 is the commercial available product whereas CAC 505 is the new commercial available optimised re-engineered pendant. Both CAC have similar chemical composition, however, CAC 505 has a slightly higher alumina content.

Mullitic fireclay phase composition was determined with 72 mass-% mullite, 14 mass-% cristobalite, 8 mass-% amorphous phases and 5 mass-% anorthite and 1 mass-% corundum. Phase composition and granulometry of both CACs are displayed in Tab. 2. Both CACs have comparable CA content and typical minor phases present. $C_{12}A_7$ is present in CA 50 with 1,6 mass-% present whereas CAC 505 has just 0,8 mass-% $C_{12}A_7$ in its composition. Differences in granulometry are obvious whereas, CAC 505 has a higher specific surface area (Blaine) and a narrower particle size distribution than CAC 50, resulting in lower d_{10} -, d_{50} - and d_{90} -value respectively.

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Keywords: calcium aluminate cement,
hibonite formation

Tab. 1 CAC and fireclay composition

Chemistry	CAC 50 [mass-%]	CAC 505 [mass-%]	Fireclay [mass-%]
L.o.I. [%]	0,1	0,5	0,1
SiO ₂	5,1	4,8	47,6
Al ₂ O ₃	50,4	51,4	48,9
TiO ₂	2,4	2,3	1,9
FeO+Fe ₂ O ₃	2,4	2,6	1,1
CaO	38,4	37,7	0,1
MgO	0,5	0,4	nd
K ₂ O	0,3	0,3	0,1
Na ₂ O	0,1	0,1	nd
Total	99,6	99,9	99,8

Tab. 2 CAC phase composition and granulometry

Mineralogy	CAC 50 [mass-%]	CAC 505 [mass-%]
CA	66,7	65,5
C ₄ AF	1,9	1,6
C ₁₂ A ₇	1,6	0,8
C ₂ AS	12,7	15,2
Pleochroite	6,1	5,8
β-C ₂ S	5,9	5,8
CT	2,6	2,9
C ₃ FT	1,8	1,9
MA	0,7	0,5
Granulometry		
Blaine [cm ² /g]	3530	4380
d ₁₀ [µm]	2,1	1,7
d ₅₀ [µm]	16,7	11,3
d ₉₀ [µm]	68,4	35,7

Tab. 3 Regular castable compositions with both CACs

Regular Cement Castable with Fireclay	CAC 50 [mass-%]	CAC 505 [mass-%]
Total CaO in castable	7,6	7,6
CAC-type	CAC 50	20
	CAC 505	–
Aggregates	Fireclay <90 µm	10
	Fireclay 0–1 mm	20
	Fireclay 1–3 mm	25
	Fireclay 3–6 mm	25
	Total	100
Added water	10,1	10,1

Both CACs were tested according to EN 14647 for water demand, initial- and final set on paste and compressive strength after 6 h and 24 h. Initial set on an EN 14647 mortar was determined with a modified

procedure according to EN196-3. Mortar design was 27 mass-% CAC and 73 mass-% quartz sand 0–2 mm, W/C = 0,4. The regular cement castable mix design is given in Tab. 3. Both castables

have the same mix composition but different types of cement. Water addition was kept constant at 10,1 % for both castables. Each castable was prepared by 4 min mixing time and the workability was determined after 5, 15 and 30 min respectively by vibrational flow according DIN EN 1402 using the cone with 50 mm height. Setting and hardening up to 24 h was recorded with ultrasonic measurement and integrated thermocouple sensor (USM, Ultratest IP-8). Permanent Linear Change (PLC) and Cold Crushing Strength (CCS) after firing at 24 h, 110 °C, 1000 °C, 1300 °C and 1400 °C were determined on prisms according to DIN EN 196 with dimensions 40 mm × 40 mm × 160 mm. Refractoriness under load was determined according to DIN EN ISO 1893 with 1 h pre-firing at 1100 °C.

Qualitative and quantitative phase analyses of the fired samples at 1000–1400 °C were performed by X-ray diffraction with a PANalytical CubiX diffractometer and data evaluation via Rietveld method, using PANalytical HighScore Plus (Version 4.6a, 2017). Amorphous content was determined by the Rietveld method with 25 mass-% quartz addition.

3 Results

Mortar and paste tests according to EN 14647 are used here to describe the general behaviour of the CAC (Tab. 4).

CAC 505 with 4380 cm²/g (Blaine) requires a somewhat higher water demand of around 1 % compared to the CAC 50 with 3530 cm²/g. CAC 50 sets faster on paste and mortar than CAC 505. Although CAC 505 has longer open time in the CEN sand mortar, 6 h and 24 h strengths are approximately 14 % higher than that of CAC 50.

When switching from EN 14647 with CEN sand mortar to refractory castables, sufficient open time for placing the castable during installation is of importance. Vibrational flow as indicator for workability is displayed in Fig. 1. CAC 50 shows a good spread of 212 mm after 5 min but flow decreases during the first 15 min to 174 mm and the castable has little workability by means of flow after 30 min. The regular castable with CAC 505 has ca. 16 % higher initial- and 40 % higher 15 min flow compared to the castable with CAC 50. The CAC 505 cast-

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Tab. 4 Tests according to EN 14647

Setting and Strength	CAC 50	CAC 505
Water demand [%]	25,6	26,6
IS Paste [h:min]	4:00	6:45
FS Paste [h:min]	4:10	7:05
IS Mortar [h:min]	2:30	3:40
FS Mortar [h:min]	2:40	3:50
6 h Compr. str. [MPa]	46,4	53,1
24 h Compr. str. [MPa]	87,0	100,1

IS: Initial set; FS: Final set

able is still workable after 30 min with a spread of 234 mm.

Hydration and hardening reaction during the first 24 h after castable mixing have been monitored by ultrasonic measurement with in situ temperature measurement (Fig. 2). Both ultrasonic curves are qualitatively similar and characterised by a period with a shallow rise, in which the velocity stays below 1000 m/s. Initial hardening is indicated by a steep increase in ultrasonic velocity and final hardening is defined by the cross section of the tangents of the curve.

CAC 50 has 77 min faster initial hardening than CAC 505 and reaches also a faster final hardening. Ultrasonic velocity of CAC 505 after 24 h is higher compared to the CAC 50. Although the ultrasonic curves are similar, the temperature measurement of both castables shows significant differences. RCC with CA 50 develops approximately 24 °C temperature directly after mixing. Temperature stays at around 24 °C during the first hour, drops then down and reaches a minimum after approximately 120 min. Temperature minimum correlates with ultrasonic initial hardening reaction of CAC 50. The 2nd temperature maximum of CAC 50 coincides with the final hardening in ultrasonic velocity curve.

CAC 505 castable temperature after mixing is lower than the CAC 50 castable temperature and stays at 21 °C for approximately 4 h. Initial hardening is indicated by subsequent temperature rise to its maximum of 25 °C after ca. 6 h. Maximum measured temperature in castable with CAC 505 is higher compared to the castable with CAC 50. The ultrasonic velocity after 24 h of castable CAC 505 is also higher than in CAC 50, indicating a higher green strength. Characteristic values of setting and hardening parameters are summarized in Tab. 5.

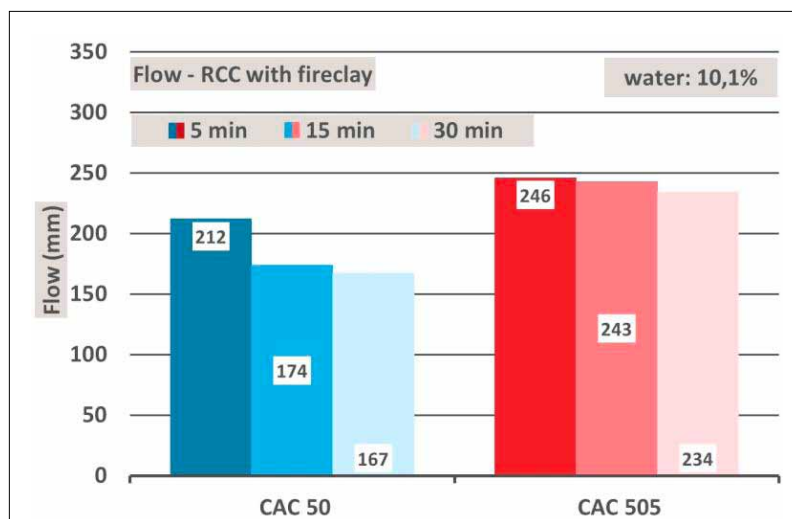


Fig. 1 Vibrational flow of RCC with CAC 50 and CAC 505

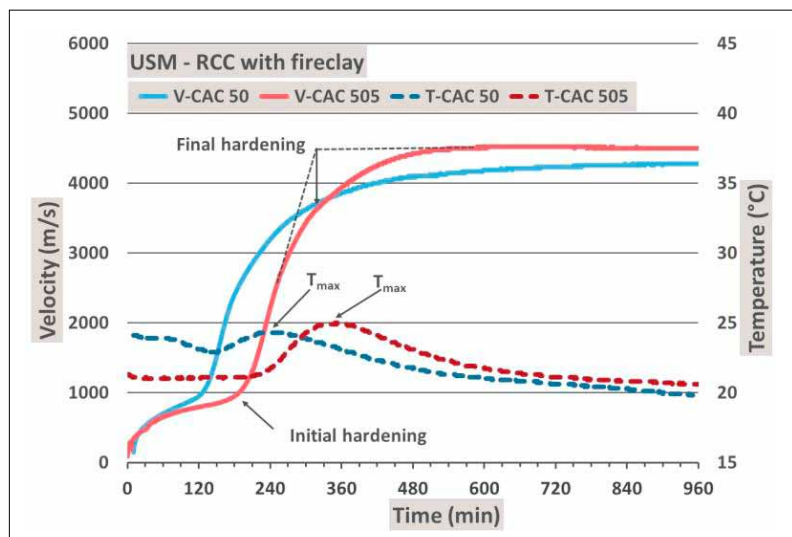


Fig. 2 Setting and hardening of RCC with CAC 50 and CAC 505

Tab. 5 Summary of setting and hardening determination methods for both castables

Method	Parameter	CAC 50	CAC 505
Ultrasonic measurement	Initial hardening [h:min]	02:05	03:22
	Final hardening [h:min]	04:00	05:18
	Δ Final – Initial [h:min]	01:15	01:56
	Max Velocity 24 h [m/s]	4300	4490
Temperature measurement	Initial hardening [h:min]	02:27	03:47
	t _{max} [h:min]	04:00	05:50
	T _{max} @ t _{max}	24,3	25,0

ening parameters are summarized in Tab. 5. CCS evolution from 24 h at 20 °C up to 1400 °C is displayed in Fig. 3. The course of strength development is similar for both

measured castables. CAC 50 has 78 MPa after demoulding. This is approximately 20 % less strength compared to the re-engineered CAC 505 castable. CCS of CAC 50 drops down to 56 MPa after dry-

ing at 110 °C. CAC 505 has approximately 26 % higher CCS than CAC 50 at 110 °C. CAC 505 reaches 47 MPa after firing at 1000 °C. This is ca. 17 % higher cold crushing strength than the castable with CAC 50. Both castables undergo a minimum in strength at 1300 °C but castable CAC 50 shows a more distinct minimum in strength than castable CAC 505. Both castables achieve nearly similar strength after firing at 1400 °C.

Permanent linear change of prisms is displayed in Fig. 4. Similar shrinkage is obtained with both castables. CAC 50 has slightly higher shrinkage than CAC 505 at 1300 °C and 1400 °C. All PLC values are lower at 1400 °C compared to 1300 °C indicating growth of expansive minerals. CAC 505 castable presents the lowest shrinkage after firing at 1400 °C.

When both regular castables are subjected to refractoriness under load (Fig. 5), qualitatively similar curves are obtained. Maximum expansion is similar but CAC 505 reaches the D_{max} at a 34 °C lower temperature than CAC 50. CAC 505 exhibits the same deformation as CAC 50 but at approximately 10 °C higher temperature than the regular castable containing CAC 50. Both castables show strong deformation after 1300 °C, but CAC 505 reaches the 5 % deformation at 1350 °C which is 15 °C higher than castable CAC 50.

Phase evolution of the RCC castables of both CAC 50 and CAC 505 after temperature treatment up to 1400 °C was analysed by X-ray powder diffraction and quantified via Rietveld method to correlate mineral changes to castable properties. Dry mix of the regular cement castable with fireclay contains 13 mass-% CA and approximately 3 mass-% gehlenite, 57 mass-% mullite, 11 mass-% cristobalite, 4 mass-% anorthite and 6,5 mass-% amorphous phase. Minor CAC phases perovskite, C3FT, larnite, brownmillerite, spinel, and pleochroite make up <4 % in the total castable mix and are referred as minor phases in the Fig. 6. Qualitative phase evolution is similar for both castables. Therefore, RCC with fireclay and CAC 505 is taken as an example to demonstrate the changes in mineralogy at selected temperatures: dry mix (20 °C) – 1000 °C – 1300 °C – 1400 °C. Calcium aluminate hydrates are already decomposed into CA and $C_{12}A_7$ at 1000 °C.

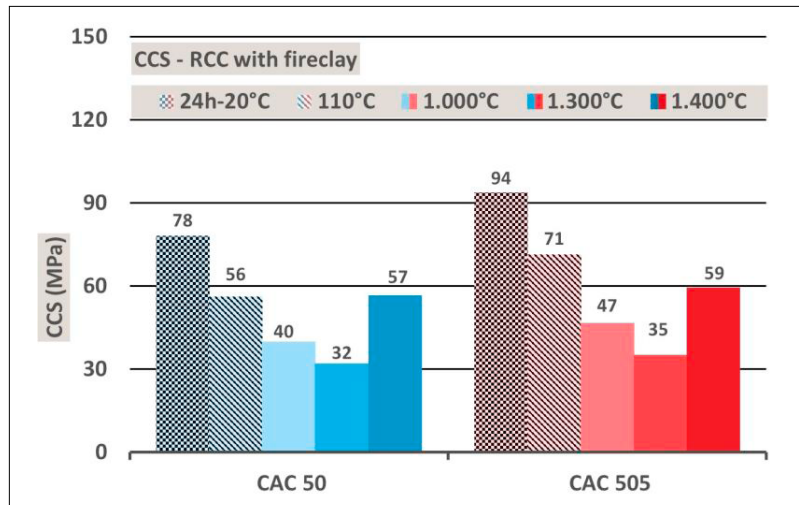


Fig. 3 Cold crushing strength after firing of RCC with CAC 50 and CAC 505

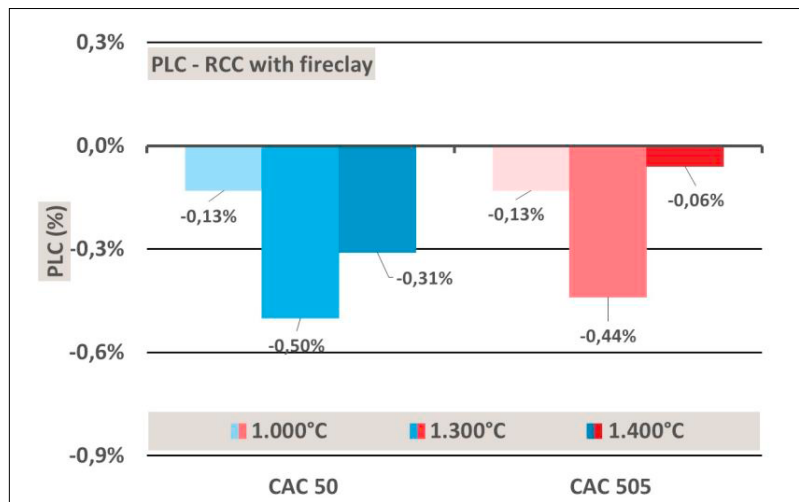


Fig. 4 Permanent linear change after firing of RCC with CAC 50 and CAC 505

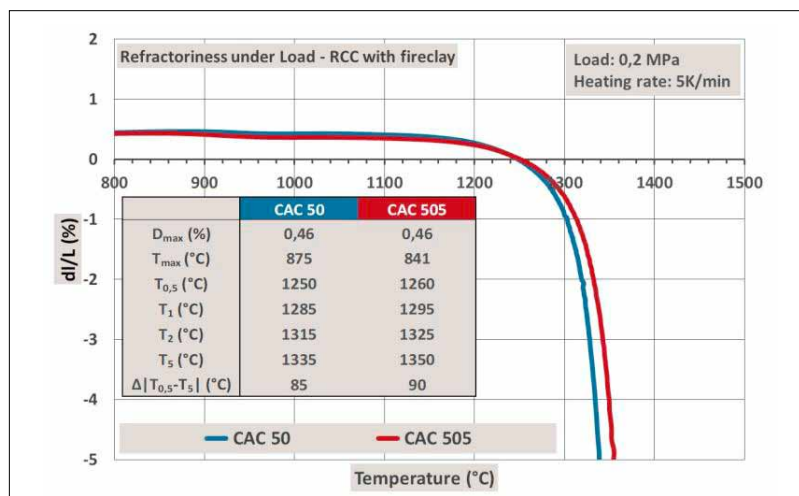


Fig. 5 Refractoriness under load of RCC with CAC 50 and CAC 505

Quantities of mullite, anorthite and corundum remain unchanged and gehlenite and cristobalite are slightly increased.

Amorphous phase decreased compared to the dry mix. This indicates a reaction of the partially depleted minor phases into

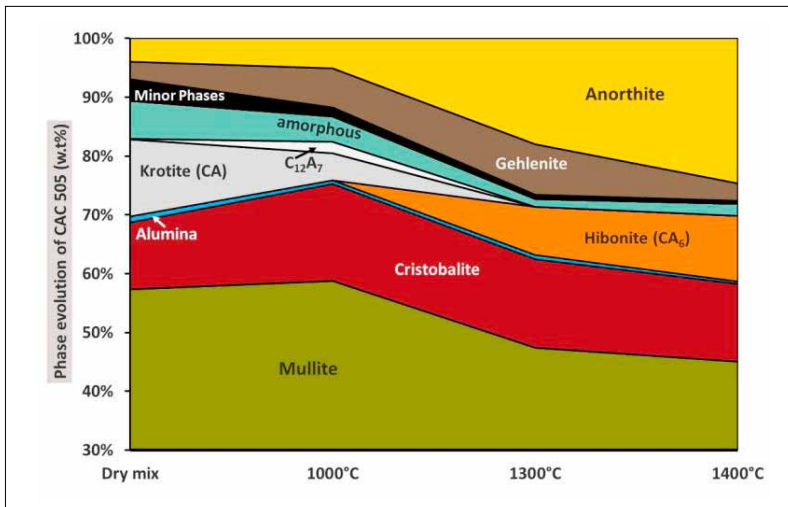


Fig. 6 Phase evolution of RCC with fireclay and CAC 505

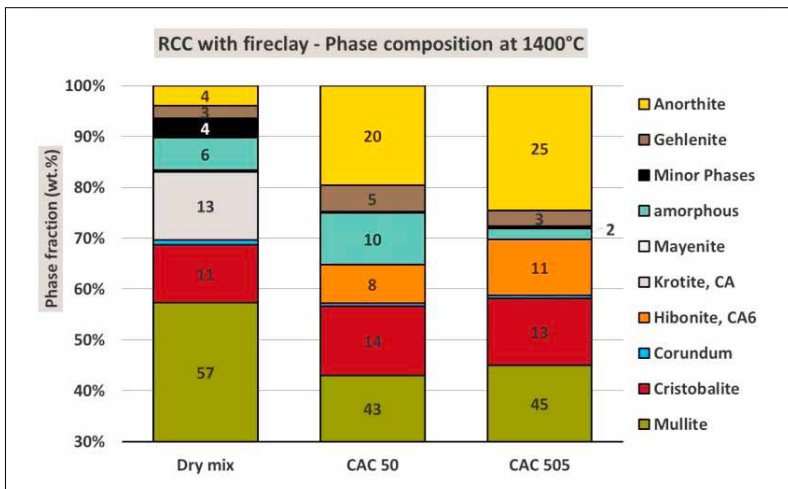


Fig. 7 Quantitative phase composition of the regular fireclay castables with CAC 50 compared CAC 505

gehlenite and cristobalite re-crystallization.

Quantitative phase composition of the 1300 °C castable reveal reactions have taken place between calcium aluminates CA and $C_{12}A_7$ with mullite and minor amounts of cristobalite. Anorthite and gehlenite content is increased compared to 1000 °C. Hibonite (CA_6) is quantified, indicating cristobalite is not sufficiently acting as silica source for this reaction at 1300 °C. Amorphous phase in the regular castable with CAC 50 is unchanged whereas the castable with CAC 505 has its amorphous phase nearly depleted.

Mullite and cristobalite amounts remain nearly constant at 1300 °C and 1400 °C whilst gehlenite is consumed and anorthite is formed. A significant difference between

both CAC containing castables is observed for the evolution of the amorphous phase. Quantification results of dry mix, CAC 50 and CAC 505 are displayed in Fig. 7. Regular cement castable with CAC 50 has 10 % amorphous phase in the mix whereas CAC 505 leads to a nearly complete crystalline phase assemblage with higher anorthite content. The hibonite content is increased by ca. 37 % compared to CAC 50 castable. The difference in amorphous contents indicates that the regular castable containing CAC 50 forms a higher amount of partial melt at 1400 °C than castable containing CAC 505.

4 Discussion

Standard tests according to EN 14647 confirm the beneficial properties of a medium

CAC with higher fineness and optimised mineralogy.

Application tests in regular cement castable with fireclay demonstrates that an already known reliable behaviour of a CAC 50 can still be improved for refractory purposes by a finer granulometry and lower $C_{12}A_7$ content, leading to the properties of CAC 505. Refractoriness under load, cold crushing strength and permanent linear change indicate that all measured properties are improved with a finer CAC at room- and high temperature.

Most remarkable improvement is the very good flow value and the gain in open time with low $C_{12}A_7$ and high specific cement surface. Vibrational flow results indicate this positive influence on a macroscopic scale but higher specific CAC surface area is superimposing the mineralogy in the flow test. Temperature and ultrasonic speed correlate very well and provide a better understanding of flow test and early hydration reactions.

The constant high temperature in the CAC 50 castable indicate $C_{12}A_7$ hydration is triggering the early CA hydration thus resulting in low vibrational flow after 30 min and rapid castable hardening. Castable CAC 505 with higher specific surface area has a longer open time in EN 14647 tests and shows flow for 30 min compared to the CAC 50.

This result can now be attributed to the low $C_{12}A_7$ content of CAC 505. Improved spread during vibrational flow of CAC 505 is therefore a direct result of the higher specific surface which leads to better material transport during flow test. Workability of CAC 505 is better, CA hydration is prolonged, but followed by a faster hydration rate, which directly results in an increased cold crushing strength.

The authors could observe this behaviour on a macroscopic scale with increased cold crushing strength after 24 h at 20 °C. CAC 50 has fast setting but approximately 20 % less strength whereas CAC 505 reaches higher strengths. CAC 505 shows higher strengths after all firing temperatures and similar or better permanent length change compared to the regular castable with CAC 50.

CAC 505's low $C_{12}A_7$ content and high specific surface lead to improved refractories under load because of a better sin-

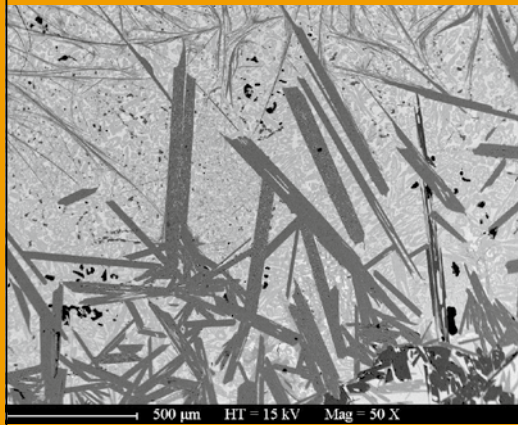
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tering behaviour, a higher crystalline phase content at high temperatures accompanied with a higher amount of hibernite for shrinkage compensation and reduced presence of liquid phase.

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