

# Strength Evolution and Corrosion Resistance of a Cement-Free $\text{Al}_2\text{O}_3$ -Castable Containing a Novel Hydraulic Binder Based on $\alpha$ -Alumina

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An alternative no-cement-binder system based on reactive  $\alpha$ -alumina and magnesia (NC-Binder) for the formulation of no cement castables has recently become commercially available under the brand name NABACAST®. A first paper has been published to describe its setting mechanism, and cold processing properties of castables containing NC-Binder [1], this second paper intends to illustrate the effect on high temperature properties of castables. It describes the use of a reactive  $\alpha$ -alumina-magnesia mix as a binder for a no cement castable and compares the properties of this castable with the properties of an ultra low cement castable. Evolution of cold compressive strength after firing at different temperatures is monitored. Slag cup tests are conducted with slags of different basicity. The results are correlated with the sintered castable's microstructure and chemical composition. Results are verified in an induction furnace test and a model of the corrosion principle is presented.

## 1 Introduction

Reduction of cement content in refractories is going on since the 1970s and has led to a significant increase in the performance of refractory castables [2]. Alternative hydraulic binders on the basis of  $\text{Al}_2\text{O}_3$  [3, 4] or MgO [5], allow the formulation of corundum based no cement castables (NCCs) that even outperform state of the art ultra low cement castables (ULCCs).

Corundum based castables free of CaO exhibit higher hot modulus of rupture and higher refractoriness under load (RUL), than those, containing CaO, coming from the addition of calcium aluminate cement (CAC) [6].

Furthermore, corrosion of  $\text{Al}_2\text{O}_3$  based refractories by metallurgical slags can be understood by the incorporation of CaO into the castables microstructure followed by a decrease of its liquidus temperature.

Once the liquidus temperature of the front layer drops below the application

temperature it melts and the chemical corrosion proceeds. CaO free refractories have a higher capacity to incorporate CaO from the slag resulting in a higher corrosion resistance [7]. Incorporation of CaO in the microstructure of alumina based refractories is followed by a volume increase due to the formation of  $\text{CA}_6$ . A dense front layer is formed which is able to retard further infiltration to some extent [8].

An innovative no cement binder system, consisting of reactive  $\alpha$ -alumina and magnesia, NABACAST® (NC-Binder) has become commercially available. Applying this binder system, the usage of hydratable transition aluminas or hydratable magnesia as a binder becomes unnecessary.

To achieve the enhanced thermomechanical properties and chemical resistance of no cement castables, refractory producers have to deal with certain draw backs resulting from the use of cement free binders, since

hydratable transition aluminas promote the risk of explosive spalling [9] and a volume shrinkage followed by drop in strength at approximately 1000 °C [4]. MgO bonded castables, on the contrary, tend to exhibit cracks caused by the volume expansion due to the formation of brucite.

The innovative NC-Binder exhibits slower setting times, compared to the other binders reported, but once dried properly at 110 °C, it does not exhibit another drawback in comparison to cement, as it was shown in a previous paper [1].

This paper intends to demonstrate the improved high temperature properties of NC-Binder in comparison to a CAC bonded castable as a prosecution of the examinations described in [1].

## 2 Experimental

### 2.1 Raw materials

Besides the binder, castables were formulated with sintered alumina aggregates (tabular alumina (TA), Alfa-Tab, Silkem/SL), calcined alumina (CA) and alumina

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**Tab. 1** Chemical analysis of alumina raw materials

	TA	CA	RA	RA
[mass-%]	all sizes	NO 135	NO 625-30	NO 713-10 MF
Al <sub>2</sub> O <sub>3</sub>	99,5	99,6	99,7	99,7
Na <sub>2</sub> O	0,3	0,3	0,1	0,1
SiO <sub>2</sub>	0,04	0,03	0,05	0,05
Fe <sub>2</sub> O <sub>3</sub>	0,08	0,03	0,03	0,03

**Tab. 2** Grain size of alumina aggregates fractions

TA					
Alfa-Tab					
[mm]					[µm]
6-3	3-1	1-0,5	0,5-0	0,3-0	45-0

**Tab. 3** Grain sizes of calcined and reactive aluminas

	CA	RA	RA
	NO 135	NO 625-30	NO 713-10 MF
D <sub>10</sub> [µm]	1,1	0,2	0,2
D <sub>50</sub> [µm]	4,7	1,7	0,9
D <sub>90</sub> [µm]	10,0	4,5	3,5

microfillers (reactive alumina (RA), NABA-LOX®, Nabaltec AG/DE). Tabs. 1–4 show the chemical and physical constitution of raw materials.

## 2.2 Castable formulation

The NC-Binder forms a relatively low amount of hydrates, during the setting pro-

**Tab. 4** Chemical and physical analysis of the binders

	NC-Binder	CAC
	NABACAST® RM 16	Secar 71
D <sub>10</sub> [µm]	0,37	0,95
D <sub>50</sub> [µm]	2,20	8,10
D <sub>90</sub> [µm]	19,50	39,60
S <sub>spec</sub> (BET) [m <sup>2</sup> /g]	7,30	1,00
Al <sub>2</sub> O <sub>3</sub> [mass-%]	89,70	69,80
MgO [mass-%]	7,40	0,12
CaO [mass-%]	0,17	29,20
Na <sub>2</sub> O [mass-%]	0,19	0,27
SiO <sub>2</sub> [mass-%]	0,56	0,25
Fe <sub>2</sub> O <sub>3</sub> [mass-%]	0,05	0,10
L.o.I. <sub>1000 °C</sub> [%]	1,86	0,18
Phase content (XRD)	α-Al <sub>2</sub> O <sub>3</sub> (+++) periclase (+) β-Al <sub>2</sub> O <sub>3</sub> (+)	Ca-monoaluminate (CA) (++) Ca-dialuminate (CA <sub>2</sub> ) (++)

cess. That is the reason why the castables have been formulated according to the approach described in [1] (Tab. 5).

## 2.3 Sample production

Castables have been poured into moulds using vibration. For CCS-measurement cylindrical moulds with a diameter of 36 mm and a height of 36 mm have been used. For the slag cup tests crucibles with an outer diameter of 50 mm and a height of 50 mm with a conical hole (depth: 38 mm, top diameter: 28 mm, bottom diameter: 25 mm) were cast.

Segments for the induction furnace test have been produced by pouring the cast-

ables into trapezoid moulds (length: 270 mm, height: 25 mm bottom width: 55 mm, top width: 75 mm). All shapes have been unmoulded after 24 h and dried for additional 24 h at 110 °C.

## 2.4 Microstructure and phase analysis

CCS-samples fired at 1500 °C and crucibles used in the slag cup test have been cut and polished for microstructural analysis (SEM and EDX, INCA-X-act, Oxford Instruments). Furthermore samples fired at different temperatures have been atomised in a vibratory mill for examination of phase evolution (X-ray diffraction, Endeavor D4, Bruker axs/DE).

## 2.5 Cold compressive strength

Cold compressive strength of the cylinders was measured according to DIN EN 196-1 : 2005-05 after drying for 24 h at 110 °C (CCS<sub>110 °C</sub>), or after firing at different temperatures (CCS<sub>400 °C</sub>, CCS<sub>1000 °C</sub>, CCS<sub>1500 °C</sub>). Bulk density was measured by geometrical means before crushing the cylinders. Holding time was 3 h for all temperatures.

## 2.6 Crucible test

The slag cup tests have been conducted with two slags of different basicity (Tab. 6). The crucibles have been sintered at 1500 °C for 2 h, before they were filled with slag and tempered for additional 3 h. Crucibles were cut into halves for evaluation of corrosion and infiltration.

**Tab. 5** Formulation of the test castables

Raw Material	K99 NCC	K99 ULCC
TA 3-6 [mass-%]	30	30
TA 1-3 [mass-%]	17	17
TA 0,5-1 [mass-%]	10	10
TA 0-0,5 [mass-%]	6	6
TA 0-0,3 [mass-%]	6	6
TA 0-45 [mass-%]	11,35	9,75
CA NO 135 [mass-%]	3,25	3,25
RA NO 625-31 [mass-%]	0	7,5
RA NO 713-10 MF [mass-%]	0	7,5
NC-Binder [mass-%]	16,49	0
CAC [mass-%]	0	3
Σ	100,09	100
PCE [g/100g]		0,09
H <sub>2</sub> O [ml/100g]	4,4	4,4

**Tab. 6** Chemical analysis and basicity factor (CaO/SiO<sub>2</sub>) of the slags

Oxide	Slag A	Slag B
CaO [mass-%]	29,1	49,4
MgO [mass-%]	1,1	3,3
SiO <sub>2</sub> [mass-%]	20,2	11,5
Fe <sub>2</sub> O <sub>3</sub> [mass-%]	35,9	4,0
Mn <sub>2</sub> O <sub>3</sub> [mass-%]	1,4	4,1
Al <sub>2</sub> O <sub>3</sub> [mass-%]	5,6	15,9
PO <sub>4</sub> [mass-%]	6,3	0,5
Rest (difference to 100 %) [%]	0,4	11,3
CaO/SiO <sub>2</sub>	1,4	4,3

**2.7 Induction furnace test**

After tempering the segments at 500 °C for 3 h the crucible for the induction furnace test was produced out of eight segments according to Fig. 1. Inside an inductive coil, filled with 12 kg of chromium-manganese-steel and heated to 1600 °C within 3 h. 750 g of synthetic slag A was added. After 1 h slag was skimmed and renewed. The corrosion test ran for 5 cycles. The segments were cut for optical evaluation of the corrosion mechanism.

**3 Results and discussion**

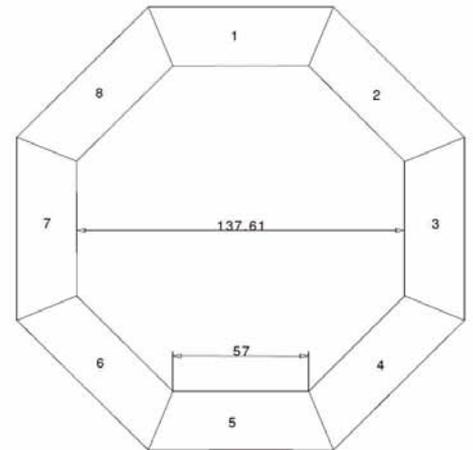
**3.1 Microstructure and phase analysis**

Fig. 2 illustrates the microstructures of the castables sintered at 1500 °C. The matrix of the CaO free castable appears finely crystalline between the tabular alumina aggregates. Not only the crystallite size, but also the pore diameter is obviously significantly finer than in the matrix of the CAC bonded castable. While the CaO content of the CAC bonded castable enforces grain growth dur-

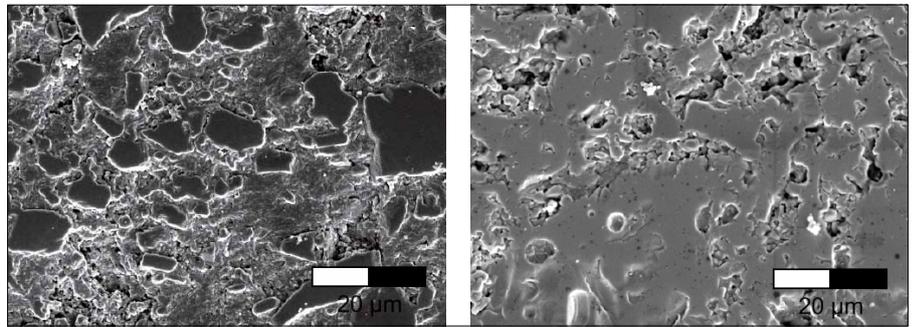
ing the sintering process, the MgO content of the castable containing NC-Binder work contrarily to that and inhibits grain growth during sintering. While the CaO containing castable forms CA<sub>6</sub>, the castable bonded with NC-Binder forms a small amount of spinel during sintering between 1000 °C and 1500 °C, as Tab. 7 indicates.

**3.2 Cold compressive strength**

Bulk density (Fig. 3) of dried samples shows a slight difference between the CAC bonded castable and the cement free castable. Due to the hydrates formed during hydration of CAC this castable exhibits a higher bulk density. The amount of hydrates formed by NC-Binder is marginal in comparison to CAC.



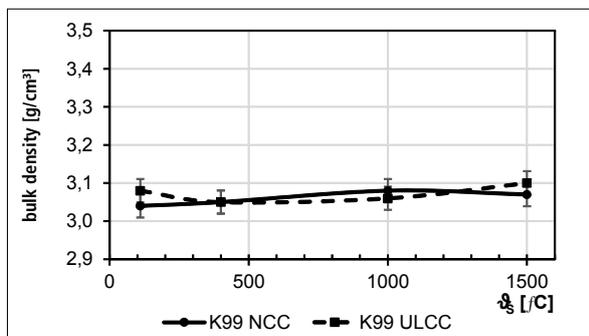
**Fig. 1** Cross section of the octagonal melting crucible



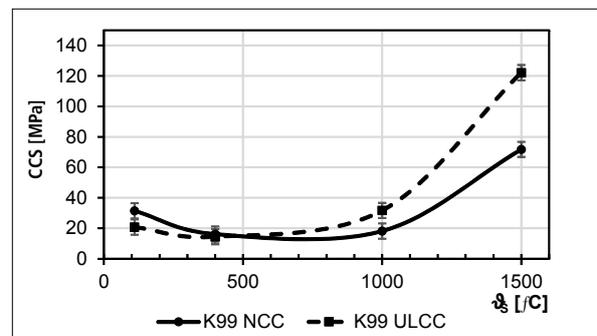
**Fig. 2** Scanning electron micrographs of the castables sintered at 1500 °C; K99 NCC (l), and K99 ULCC (r.)

**Tab. 7** Phase content of the castables containing NC-Binder or CAC depending on the sintering temperature  $\vartheta_s$ , according to XRD analysis

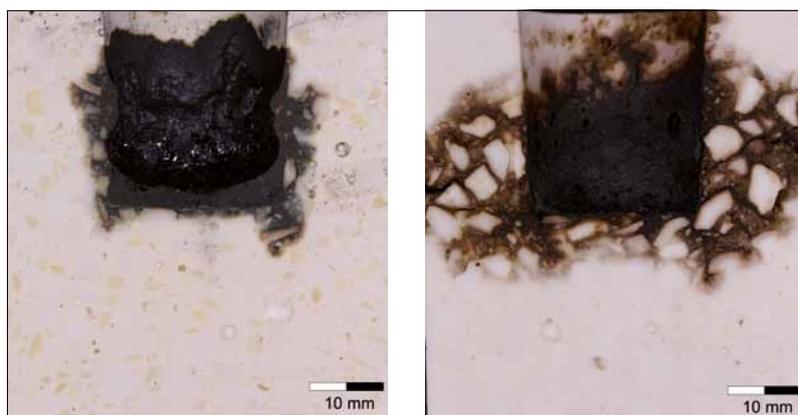
$\vartheta_s$ [°C]	K99 NCC				K99 ULCC			
	110	400	1000	1500	110	400	1000	1500
Periclase	+	+	+					
Spinnell				+				
$\beta$ -Al <sub>2</sub> O <sub>3</sub>	+	+	+	+	+	+	+	+
Corundum	+++	+++	+++	+++	+++	+++	+++	+++
CA <sub>6</sub>								++
CA <sub>2</sub>						+	+	
CA						+	+	



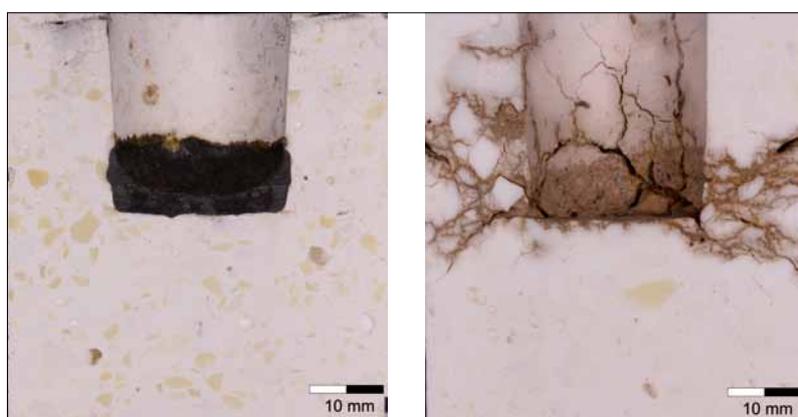
**Fig. 3** Development of bulk density in dependence of the sintering temperature ( $\vartheta_s$ ) of castables bonded with NC-Binder or CAC



**Fig. 4** Development of cold compressive strength (CCS) in dependence of the sintering temperature ( $\vartheta_s$ ) of castables bonded with NC-Binder or CAC



**Fig. 5** Sections of slag cup tests with slag A at 1500 °C; K99 NCC (l.), and K99 ULCC (r.)

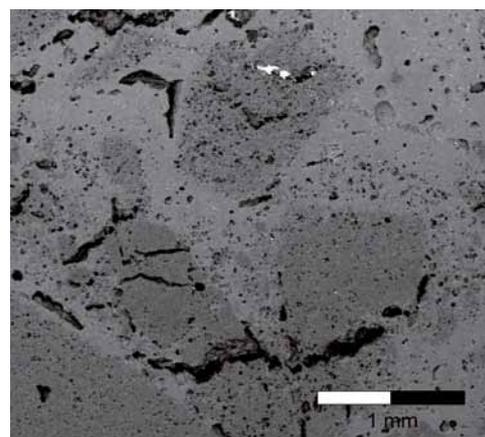


**Fig. 6** Sections of slag cup tests with slag B at 1500 °C; K99 NCC (l.), and K99 ULCC (r.)

After decomposition of hydrates at 400 °C bulk density of the CAC bonded castable drops to the level of the castable containing NC-Binder and even after firing at 1000 °C, there is no difference measurable.

A low sintering shrinkage at 1500 °C results in a slight increase of bulk density for the CAC-bonded castable, while the CaO-free castable still remains on the level as before. Fig. 4 illustrates strength evolution of the castables. For dried samples, CCS of the

castable containing NC-Binder is with 32 MPa higher than for the CAC bonded castable (21 MPa). It has to be mentioned that both castables have been formulated with a deflocculant optimised for NC-Binder, which may lead to abnormal growth of hydrate crystallites during the hydration of CAC. If a commercial deflocculant (Repac 200, Kerneos/FR) is applied, dried strength of the CAC bonded castable can be measured with 48 MPa. After decomposition of

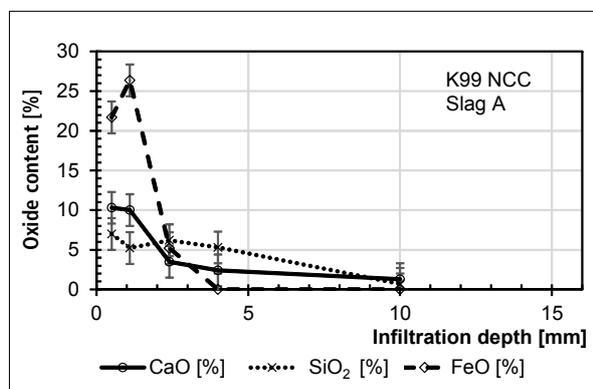


**Fig. 7** Scanning electron micrograph of slag cup tests with slag A, and K99 ULCC at 1500 °C

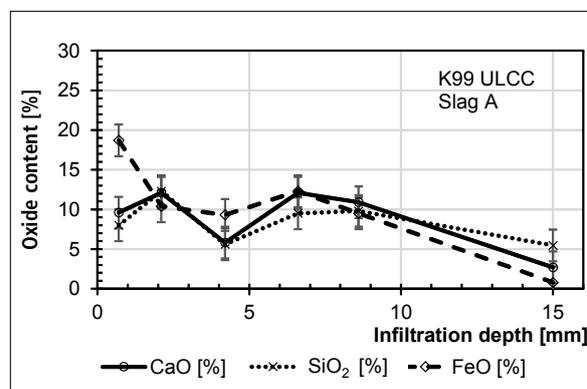
the hydrates, CCS of both castables drops to the same level. Strength increases starting at 1000 °C due to sintering effects, while it can be seen, that the CaO containing castable shows its sintering effects at lower temperatures. Lower level of CaO and higher temperature resistance of the CaO free castable results in less microstructural changes, such as phase transformations and crystal growth at the same sintering temperature.

### 3.3 Slag resistance

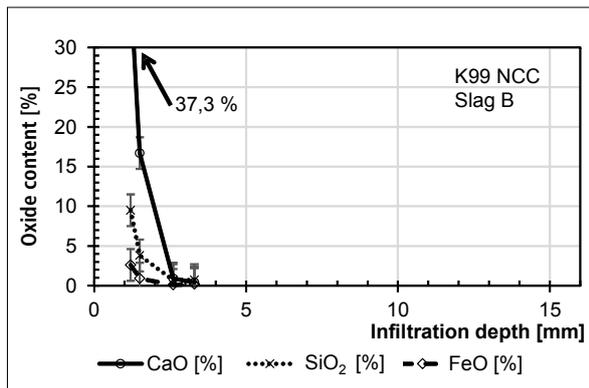
Both, the slightly basic slag A (Fig. 5), as well as the strongly basic slag B (Fig. 6) penetrated completely into the CAC bonded crucibles until no slag bath remained. The reaction between refractory material and slag caused a significant volume expansion leading to massive cracking of the crucibles. This volume expansion is likely related to the formation of  $CA_6$  out of  $Al_2O_3$  from the refractory material and CaO from the slag.



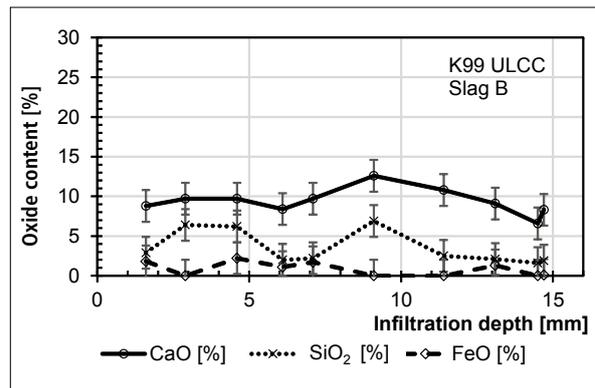
**Fig. 8** Concentration of slag A elements in the castable matrix of K99 NCC in dependence of the infiltration depth



**Fig. 9** Concentration of slag A elements in the castable matrix of K99 ULCC in dependence of the infiltration depth



**Fig. 10** Concentration of slag B elements in the castable matrix of K99 NCC in dependence of the infiltration depth



**Fig. 11** Concentration of slag B elements in the castable matrix of K99 ULCC in dependence of the infiltration depth

The CaO free castable containing NC-Binder was infiltrated much less by both slags. After a few millimeters, infiltration stopped and a slag bath remained in the crucibles, allowing some corrosion at the contact zone between refractory material and slag. Fig. 5 shows the infiltration running via pathways that take course between the tabular alumina aggregates in the matrix of the castable. Those pathways can also be recognised in SEM pictures (Fig. 7) as zones of coarser crystallinity and coarser porosity. Apart from that infiltration pathways appear brighter in the back scattered electron mode of the SEM due to their higher iron content. In order to understand the mechanism of infiltration retardation, the chemical composition of infiltrated castable matrix was determined by EDX in different distances from the corrosion front. Fig. 8–11 illustrate how the concentrations of slag elements decrease in the castable matrix depending on the depth of infiltration into the castable.

It can be seen that both slags have been able to penetrate through the microstructure of the CaO containing castable quickly and without a significant reaction between slag and refractory material that could cause a retardation of infiltration. Unlike this, infiltration of the slags into the CaO free castable is retarded in a very early stage and stops after approximately 10 mm for slag A and after 3 mm for slag B, respectively. Fig. 8 shows the CaO concentration dropping after 1,2 mm of infiltration, while SiO<sub>2</sub> was able to penetrate 4 mm. The drop of CaO content is likely related to the formation of CA<sub>6</sub> in the front layer. The volume expansion coming along with this phase transformation hinders slag propagation, but is probably not high enough to stop

the remaining slag completely from further penetrating. Due to the high FeO content, the viscosity of the remaining slag is still low enough to infiltrate few millimeters more. At 4 mm also FeO drops to zero, which is likely related to the effect of spinel. The more basic slag B completely stops penetration once the CaO has been absorbed by the ce-

ment free castable matrix, simply because the content of SiO<sub>2</sub> and FeO is much lower in that slag. It can be derived that the CaO free castable has a higher CaO absorption capability due to its higher purity and its finer crystallinity. Slag infiltration is retarded by an increase of slag viscosity and densification of the microstructure. The finer pore

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**NABACAST®** is a novel hydraulic binder that reacts with water under the formation of hydrates, which causes consolidation of the refractory concrete.

### Micro-filler

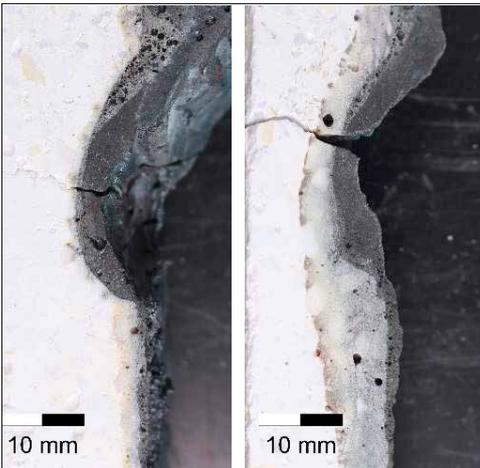
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**Fig. 12** Cross sections of the segments used in the induction furnace test: K99 NCC (l.), and K99 ULCC (r.)

size distribution of the CaO free castable is another, physical reason for slower infiltration of any slag.

Fig. 12 shows the cross sections of the segments used in the induction furnace test.

On the one hand it illustrates that only the CaO containing castable is infiltrated which confirms the results of the slag cup tests. On the other hand the corrosion of refractory material is on the same level for both castables. Chemical corrosion of the refractory material is caused by solution of  $Al_2O_3$  in the slag which happens directly at the solid-liquid interface. Tabular alumina aggregates are attacked in the same manner as the matrix of the castables.

#### 4 Summary

It could be shown that a tabular alumina based castable bonded with NC-Binder instead of CAC shows a similar strength evolution during the first heating up, while sintering effects occur only at a temperature approximately 150 °C higher.

The sintered castable contains a small percentage of spinel instead of  $CA_6$  and exhibits a microstructure with finer pore size distribution. Due to this not only FeO

but also CaO is absorbed by the castable's microstructure at very early stages of infiltration which leads to a significant advantage of the NC-Binder containing castable in terms of slag infiltration resistance. The mechanism is the same for slags of different basicity and will lead to a higher service life of refractories containing NC-Binder in contact with metallurgical slags.

#### 5 Outlook

From literature and from own measurements it is known that RUL of tabular alumina based ULCCs can already exceed 1700 °C, which is the range limit of the usual test bench. A CaO free castable should exhibit even higher RUL, simply for thermodynamical reasons. The experimental prove of this phenomenon is subject of future works.

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Reactive Aluminas

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