

MINERALOGY AND MICROSTRUCTURE EVOLUTION ALONG THE CURING, DRYING AND FIRING PROCESS OF CALCIUM ALUMINATE BONDED REFRACTORY CASTABLES

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Abstract

Refractory castables are semi-finished products when supplied as dry-mix to the end-user. Therefore the knowledge about aspects like mineralogy, phase transformation and micro-structural changes starting from castable wet mixing up to the first heat-up is crucial not only for the producer of the refractory mix but also for the service companies responsible for installation, curing, drying, and heat-up. This paper reviews the principle phase reaction mechanisms and explains the impact on the microstructure during this part of the life cycle of a high purity refractory castable. Furthermore the impact of three different Calcium Aluminate binders has been studied. SECAR[®] 71 is a 70% alumina containing binder while SECAR[®] 80 and SECAR Plenium[®] are 80% alumina binders. With SECAR Plenium[®] the lowest water demand, lowest porosity, highest strength and a sub-micron micro-pore system has been achieved. Mineralogical changes in the microstructure during the first castable heating are steadier with SECAR Plenium[®] than with the 70% alumina cement. The high temperature resistant phase CA₂ is the main CaO containing phase at 1100°C while in the case of SECAR[®] 71 still a significant amount of CA is present at this temperature. In traditional Regular Castables (RC) a weak zone occurs at 1100°C when the castable is exposed to a temperature gradient. The strength at 1100°C is significantly lower than at 500-800°C or at 1350°C. With SECAR Plenium[®] the strength is boosted significantly so that also at 1100°C sufficient strength levels can be achieved. Overall it has been demonstrated that SECAR Plenium[®] offers a range of advantages over traditional 80% and 70% alumina cements. High strength, low porosity and a submicron pore system are some of the characteristics. It has to be mentioned here that the very small micro-pore diameters have been achieved without any microsilica or reactive alumina addition to the formulation nor addition of deflocculants. SECAR Plenium[®] offers therefore significant improvements in areas where the castable is in contact with ferrous or non-ferrous metal but also in fields where a high abrasion resistant silica-free castable is required throughout a large temperature range. The high purity microstructure and the up to 100% higher strength compared to a 70% alumina cement makes SECAR Plenium[®] not only interesting for applications in the steel industry like in steel ladles but as well in the temperature range between 800 and 1100°C for example in applications with direct contact to non-ferrous metals like aluminium and copper.

1 Introduction

Joint free furnace linings, the engineering of very complicated shapes, and short delivery times are some of the advantages achievable with refractory castables compared to brick linings. Refractory castables have found their application fields both, in metallurgical and non-metallurgical industries. Calcium Aluminate Cement (CAC) based castables are competitive alternatives to bricks in all of these areas. To reach the optimal performance level out of a castable that has been supplied as a dry-mix to the job side, not only the quality of the dry-mix itself but also the quality and accuracy of the installation, curing, drying and heat-up are essential. The knowledge and understanding of the mineralogical and micro-structural evolution during these steps are crucial to transform the dry-mix into a high performance, solid monolithic construction ready to use in the targeted furnace. These steps have to be seen as part of the production process of the refractory castable. By studying the impact of formulation changes on the mineralogical and micro-structural evolution during castable mixing, curing, drying and heat-up, space for potential improvements can be detected and can lead to new developments. In the following paper, the impact of different calcium aluminates on the mineralogy and microstructure will be discussed. Three different high-purity CAC's have been chosen to demonstrate how small changes in the formulation can strongly impact and improve the properties of the product and broaden their scope of application. SECAR® 71 is a pure 70% alumina cement while SECAR® 80 and SECAR Plenium® are both composite cements with 80% alumina and an integrated additive system. These 3 calcium aluminate binders have been used at an addition rate of 15% in the model system as shown in Tab. 1. Each mix has been tested without and with the addition of Polypropylene fibres.

Tab. 1: Model castables

AT15		Secar 71	Secar 71 fibre	Secar 80	Secar 80 fibre	Secar Plenium	Secar Plenium fibre
Raw material		wt%	wt%	wt%	wt%	wt%	wt%
Tabular alumina	1/4-8 mesh	32	32	32	32	32	32
Tabular alumina	8-14 mesh	15	15	15	15	15	15
Tabular alumina	14-28 mesh	10	10	10	10	10	10
Tabular alumina	28-48 mesh	13	13	13	13	13	13
Tabular alumina	-48 mesh	10	10	10	10	10	10
Tabular alumina	-325 mesh	5	5	5	5	5	5
Secar 71	4000 m ² /g	15	15				
Secar 80	9000 m ² /g			15	15		
Secar Plenium	11000 m ² /g					15	15
PP-fibre	6 mm/14 µm		0.1		0.1		0.1
H2O		8	8.5	6.7	7.2	5.9	6.4
Initial Vibration Flow (%)		102	88	99	87	100	84

2 Test methods

The formulations have been mixed with an amount of water in a Hobart-like laboratory mixer during 4 minutes so that a vibratable consistency could be achieved with an initial vibration flow of ca. 80 to 100%. An ASTM-cone was used and a vibration time of 20 sec and amplitude of 0.5 mm. After casting into steel moulds of 3x3x16 cm³ the samples have been stored during the first 24h at 20°C and >90% relative humidity prior to drying at 110°C during 24h followed by firing at higher temperatures during 6h. Castable permeability has been tested with an apparatus as described by [1]. Open porosity has been measured by water immersion. The pore size distribution, measured by mercury intrusion and the mineralogical evolution during curing, drying and heating has been determined on the matrix part of the castable only. The composition and water/cement-ratio of this matrix part is shown in the Tab. 2. The phase quantification has been carried out using the Rietveld method [2]. However, it has to be mentioned that non-crystalline phases that can occur during the curing of the castable can't be detected with this method. Therefore these samples have been studied as well with a Differential Scanning Calorimeter (DSC).

Tab. 2: Composition of matrix mortar

		S71	S80	S PI
Tabular alumina	-48 mesh	33.3	33.3	33.3
Tabular alumina	-325 mesh	16.7	16.7	16.7
Secar 71	4000 m ² /g	50		
Secar 80	9000 m ² /g		50	
Secar Plenium	11000 m ² /g			50
H2O		25	18	16
Water/Cement ratio		0.50	0.36	0.32

3 Test results

First interaction between the dry-mix and mixing water

A proper mixing time has to be chosen in order to fully wet-out and disperse the powder of the dry-mix in order to achieve a homogeneous castable. 4 minutes wet mixing time has been chosen, although wet-out was visibly achieved after around 30-45 seconds in all cases. As can be seen in Fig. 1 the necessary water addition to achieve an initial flow between 180 and 200 mm can strongly be reduced by replacing SECAR[®] 71 with SECAR[®] 80 and even further down by using SECAR Plenium[®]. This is the impact of an optimized granulometry and a tailored admixture package in the composite cements, especially in SECAR Plenium[®]. When polypropylene fibres are used a slightly higher water addition is necessary in order to achieve the targeted initial vibration flow.

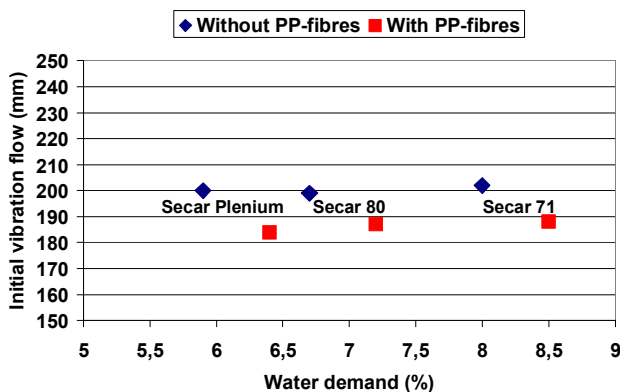


Fig. 1: Water addition to castable to achieve a the targeted initial vibration flow of 18-20%

At the moment of water addition the clock for chemical reactions starts to tick as the cement

powder begins to dissolve in the mixing water. However, solubility of calcium aluminate is relatively low so that not all cement can dissolve immediately in the pore solution. Typically the pore solution is quickly saturated with Ca²⁺ and/or Al(OH)₄⁻ ions which slows down further cement dissolution till the moment when massive cement hydration starts [3].

Phase evolution during curing at 20°C and drying at 110°C

Between the moment of saturation and the massive hydrate precipitation a lengthy time can pass during which the system is in a kind of dormant period as described for example in [3]. In the case of SECAR[®] 71 this effect is quite visible. In Fig. 2 the evolution of the main anhydrous cement phases CA and CA2 in the matrix mortar is shown. No significant change in the amount of anhydrous cement phases has occurred 4h after water addition. During 24h curing at 20°C, 50% of the initial CA content has been dissolved and transformed into hydrates but almost all CA2 is still present. Then, during dry-out at 110°C most of the CA as well as the CA2 have been consumed. With SECAR[®] 80 and SECAR Plenium[®] the reaction path is slightly different. As can be seen for SECAR Plenium[®] in Fig. 3 a considerable amount of CA and of some CA2 have started to dissolve already after 4h and after 1d nearly 2/3 of the initial CA content are transformed.

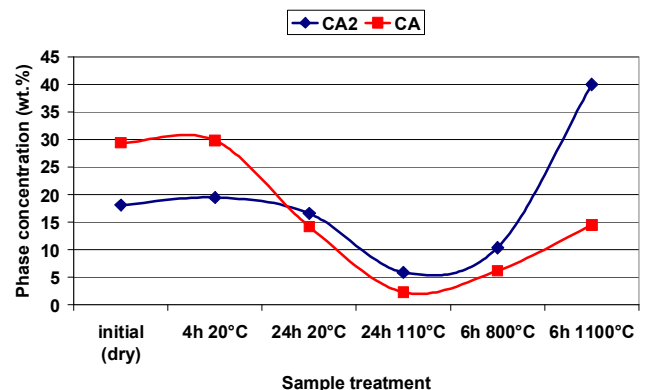


Fig. 2: CA and CA2 in matrix mortar with SECAR[®] 71

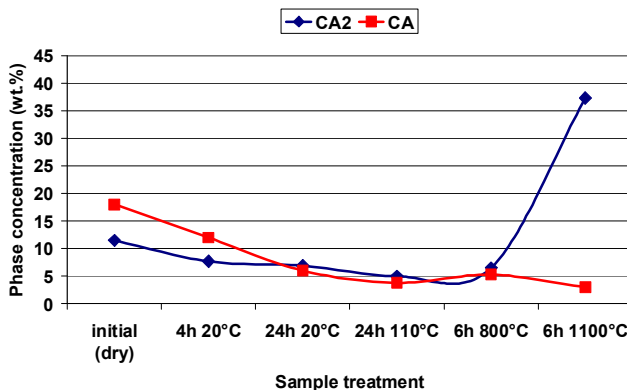


Fig. 3: CA and CA2 in matrix mortar with SECAR Plenium®

In Fig. 4 and 5 it can be seen that after 4h SECAR® 71 has not yet formed hydrates that are detectable by XRD. But DSC tests show that some hydrate-gel is already present which explains that the mix has stiffened already at this point. In the mix with SECAR Plenium® a considerable amount of Gibbsite has been detected already after 4h. Curing up to 24h creates much more Gibbsite than in the case of SECAR® 71. CAH10, the meta-stable CA-hydrate that forms typically at low ambient temperatures [4] has been found in significant amount after 24h at 20°C in case of SECAR® 71 while only traces have been detected when SECAR Plenium® was used. After drying at 110°C all CAH10 has been converted in all cases into the stable hydrate C3AH6 and further Gibbsite while the water which is released during this conversion process has supported at this temperature the hydration of the less reactive CA2. Also most of the gel-phases that have been detected after 24h curing at 20°C in the DSC analyses have been transformed into crystalline hydrates of AH3 and C3AH6.

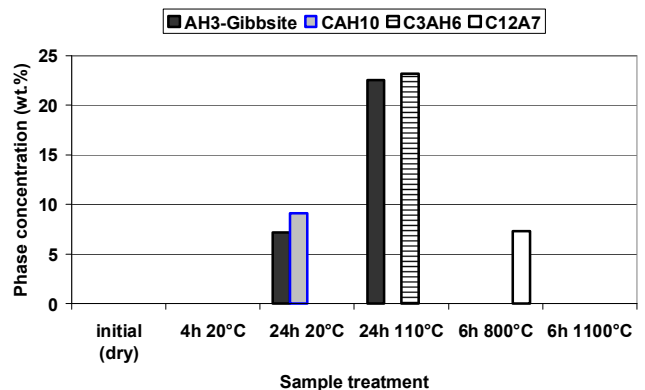


Fig. 4: Hydrates and appearance of C12A7 during first heat-up in case of SECAR® 71

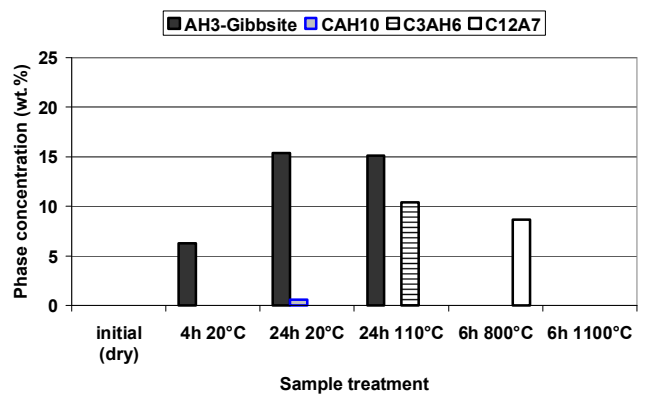


Fig. 5: Hydrates and appearance of C12A7 during first heat-up in case of SECAR Plenium®

Although SECAR Plenium® forms a smaller quantity of hydrates compared to SECAR® 71 it reaches significantly higher strength after drying at 110°C. Both, CMOR and CCS are 30 to 50% higher for SECAR Plenium® (Fig. 6-9). The reason for this can be found in the fact that SECAR Plenium® can be cast with significantly less water compared to Secar® 71 which gives a much more dense structure and lower open porosity (Fig. 10 and 11). Furthermore, SECAR Plenium® has a much higher specific surface area which allows a better particle packing and results in a much finer pore size distribution (Fig. 12 and 13)

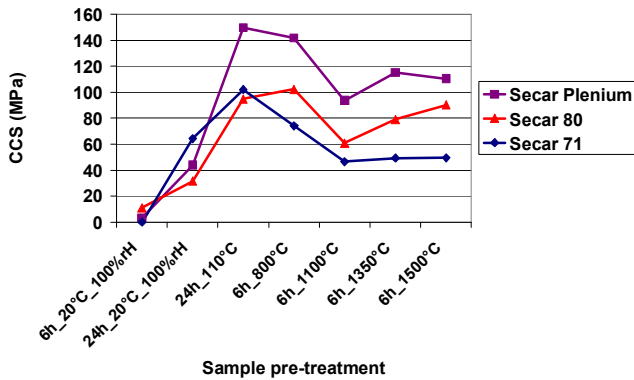


Fig. 6: CCS of castable without Polypropylene fibre

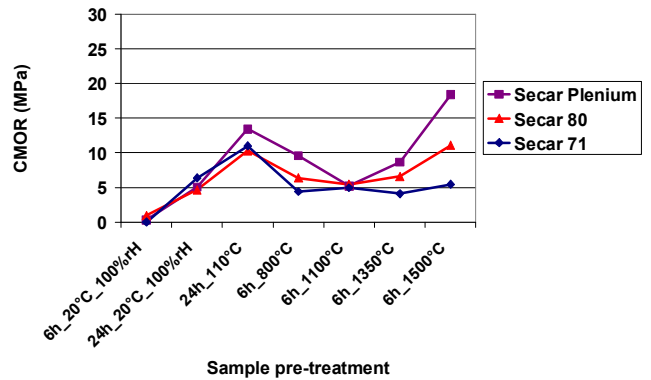


Fig. 9: CMOR of castable with Polypropylene fibre

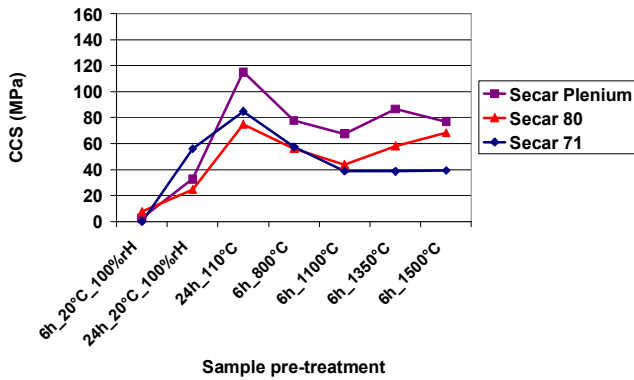


Fig. 7: CCS of castable with Polypropylene fibre

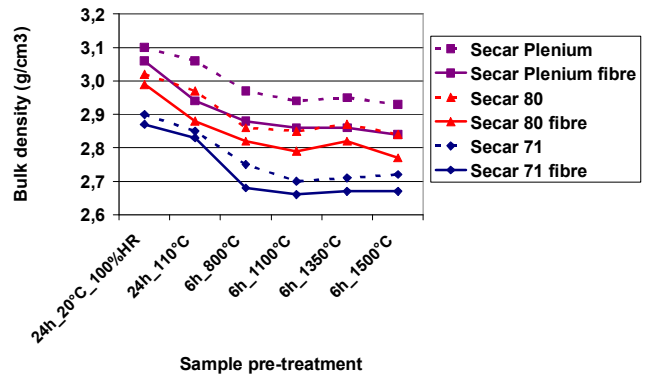


Fig. 10: Bulk density evolution of castables

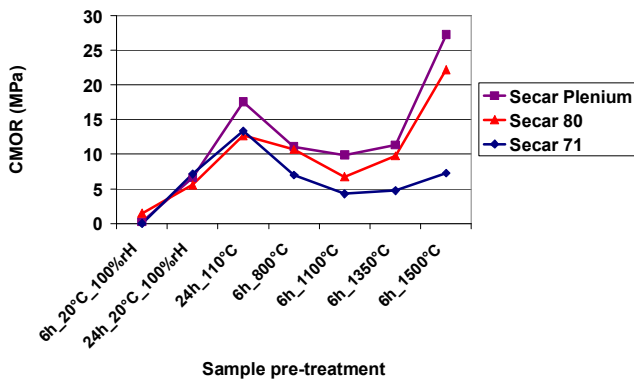


Fig. 8: CMOR of castable without Polypropylene fibre

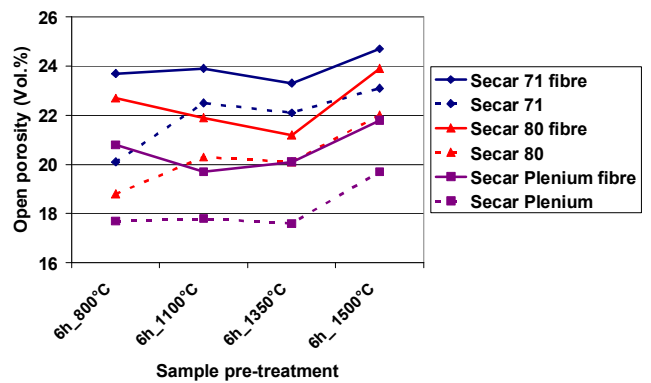


Fig. 11: Evolution of open porosity of castables

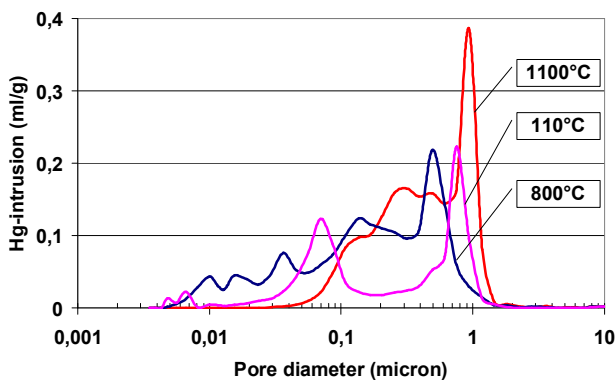


Fig. 12: Pore size distribution of matrix mortar with SECAR® 71

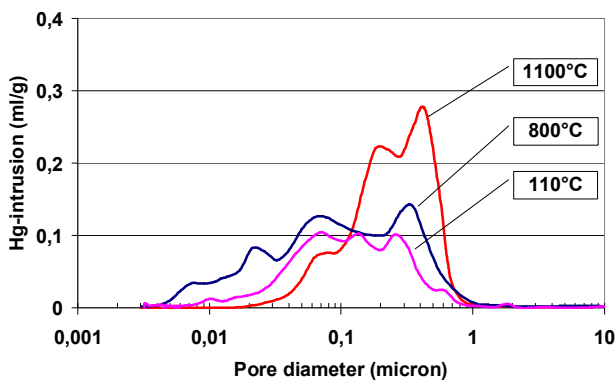


Fig. 13: Pore size distribution of matrix mortar with SECAR Plenium®

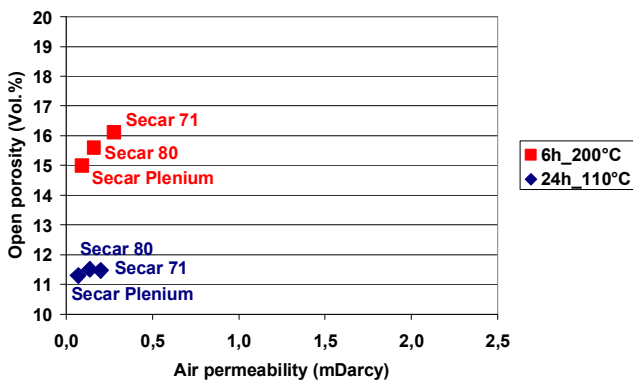


Fig. 14: Open porosity and permeability for castable without Polypropylene fibre

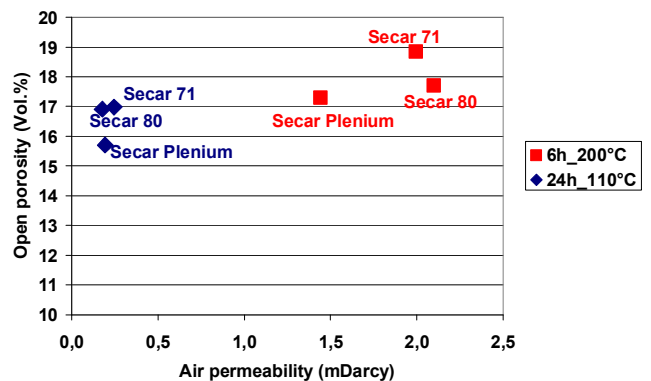


Fig. 15: Open porosity and permeability for castable with Polypropylene fibre

First heat-up from 110°C to application temperature

During the heating process most of the chemically bonded water is released between 150 and 350°C. Since different hydrates are present the reaction doesn't appear at once. For example, it can be concluded from DSC measurements that CAH10 starts to decompose at ca. 140-150°C, the crystalline AH3, Gibbsite de-hydrates at ca. 250°C-270°C and C3AH6 when ca. 300°C are reached. If the permeability of the microstructure is sufficiently high enough to transport the water as steam easily from the centre to the surface of the monolith then no hydrothermal conditions will exist. Hydrothermal conditions would favour the formation of hydrates that could be stable even up to 500°C like AH, Boehmite [1]. Therefore the addition of permeability enhancers like PP-fibres is generally recommended. The effect on air permeability is clearly visible in Fig. 14 and 15. Somewhat surprisingly, although the open porosity at 110°C is lower when no PP-fibres are added as consequence of the lower water demand, the relative increase in porosity is higher between 110°C and 200°C than when fibres are present. Therefore the difference in porosity between the fibre-containing and the fibre-free mix is relatively small at 200°C while the advantage of PP-fibres is clearly visible in the air permeability values.

SECAR Plenium[®] combined with PP-fibres results in a higher strength level over all temperatures than in case of SECAR[®] 71 without PP-fibre. It also seems that the typically weak zone that occurs for this type of Regular Castable (RC) in the temperature range around 1100°C (Fig. 6 and Fig. 8) is less significant when PP-fibre was used in the mix. However this needs to be investigated further.

Between 300 and 800°C, the de-hydrated phases are initially poorly crystallized but there is some evidence that they start to re-crystallize in form of transition aluminas like gamma-Al₂O₃. Also it seems that the de-hydration product of C3AH6 incorporates as temperature increases some alumina which results in the formation of C12A7 which has been detected by XRD at 500 and 800°C in the matrix mortar both for SECAR[®] 71 and SECAR Plenium[®] (Fig. 4 and 5). As higher temperatures are reached, SECAR[®] 71 and SECAR Plenium[®] react differently. In case of SECAR[®] 71 both CA and CA2 occur in significant amounts at 1100°C (Fig. 2). With SECAR Plenium[®] all the lime that was present in the cement has been already transformed into the higher temperature resistant CA2-phase (Fig. 3). The less temperature resistant phase CA is already nearly completely consumed at this temperature. As temperature increases further CA2 in case of SECAR Plenium[®] and CA2+CA in case of Secar 71 can continue to react to form the high temperature resistant phase CA6 if enough alumina is present in the system. SECAR[®] 80 and SECAR Plenium[®] contribute only 3% lime to the castable when a 15% CAC addition is used. This results after full reaction into a castable with approximately 37% CA6 and 63% A. This means that the full matrix of this castable can be transformed into CA6 at sufficiently high temperatures, for example at 1500°C. In case of 15% SECAR[®] 71 in the concrete, the CaO content would be 4.5%. This would have a potential to create 54% CA6. However, in that case some of the coarser fractions of tabular alumina have to

participate in the reaction which effectively slows it down so that it becomes more difficult to reach the thermodynamic equilibrium. As consequence the matrix will remain for a longer time in a slightly lime oversaturated status compared to the thermodynamic equilibrium. Therefore with SECAR Plenium[®] a stable CA6-A regime can be achieved more quickly. With the CA6-A system an excellent hot strength and thermal shock resistance can be achieved. Furthermore, SECAR Plenium[®] has a lower level of impurities than SECAR[®] 80 with a lower level of alkalis. Alkalis would be transformed into beta-alumina which has a lower density than alpha-alumina and consequently creates a permanent thermal expansion. SECAR Plenium[®] forms at 1500°C only small amount of beta-alumina which is important for a high volume stability of the monolith.

4 Summary and conclusion

The investigation has shown that a series of chemical and ceramic reactions occur from castable mixing with water right up to the moment when the castable can be used for the first time in a furnace. A significant improvement of the microstructure has been achieved by using SECAR Plenium[®] in this high purity castable. This results in very low porosity, very small pore diameters and excellent strength values. The formation of phases in SECAR Plenium[®] at 1100°C favour a microstructure that resists high temperatures, reduces the penetration of ferrous and non-ferrous metals like aluminium and copper. With SECAR Plenium[®] an extraordinary high strength level has been achieved at relatively low application temperature of 800°C. This makes SECAR Plenium[®] also interesting in lower temperature applications like in aluminium furnaces where high strength is an important aspect. This can be achieved with a high purity silica free Regular Castable concept, without the need to add fume silica or alumina fillers nor deflocculants.

At very high application temperatures like in steel ladles, burners, lances etc SECAR Plenium® offers an excellent stability due to the fast formation of the A-CA2 resp. CA6 system. These calcium aluminate phases have a low thermal expansion so that combined with the micro-porous microstructure an excellent thermal shock resistance can be expected.

5 References

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