Improvement of Refractory Castables with an Innovative Calcium Aluminate Binder System

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The properties and performances of refractory castables depend not only on the type and amount of calcium aluminate cement (CAC) that is used, but is greatly influenced by the interaction between the cement and the chosen aggregates for a given system. The cement interacts not only with the fine aggregates, but also with reaction partners that may be present in the binder system such as alumina, microsilica as well as various admixtures. The optimization of this complex system is essential for the rheological setting and refractory properties of the castable.

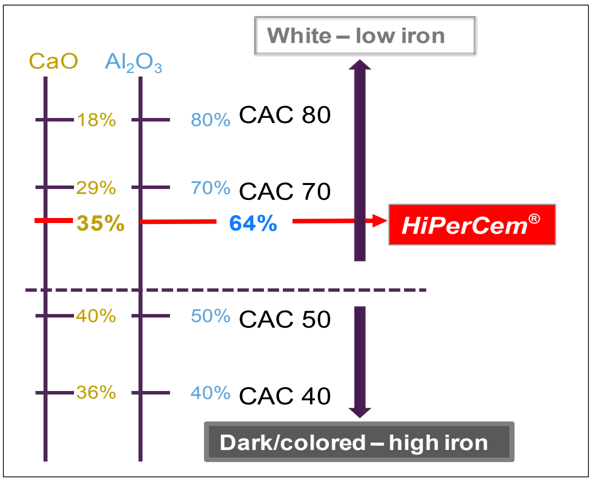

Fig. 1 Segmentation of calcium aluminate cements

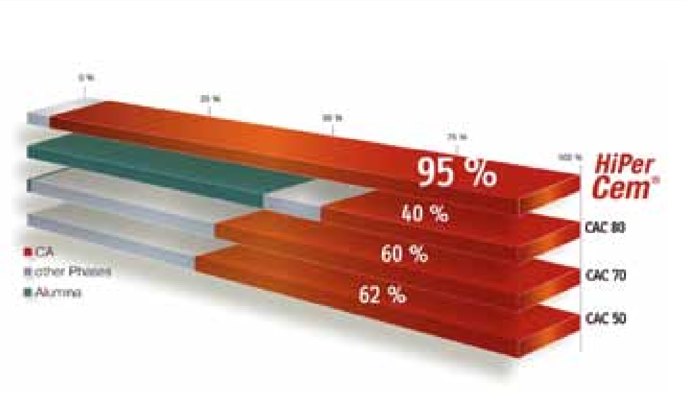

Fig. 2 Monocalcium aluminate content of CA cements

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1 Calcium aluminate cements and their role in refractory castables

Due to technological developments in recent years, CAC with an alumina content of approx. 70 % and CaO of 30 % play a major and important role in the formulation of the so-called formulated castables, which are subdivided depending upon the CAC content into medium – low – ultra-low cement castables. There is a range of other CAC available, which play a minor role in refractories, especially with a view to high tech materials (Fig. 1).

The major reactive phase in the CAC is monocalcium aluminate (CA), which produces the short-term hydraulic properties that are desired and necessary in a castable. Other CA-phases, such as CA_2, react very slowly and when the target is in many cases a short installation and heat-up time, these additional phases do not contribute to the hydraulic reactivity and represent only an additional amount of CaO in the chemical composition of a castable. This leads, in most cases, to higher amount of lower melting feldspar phases, which deteriorate the refractory properties and increase the sensitivity of slag attack and corrosion at high temperatures.

Another unique property is the special particle size distribution, which is much steeper than with standard CAC. This property is expressed by the slope *n*, which is shown in Fig. 3. The purpose of this adjustment is to minimize the interference that HPC has with the reactants in the binder system, which in most cases are finer and have thus a better

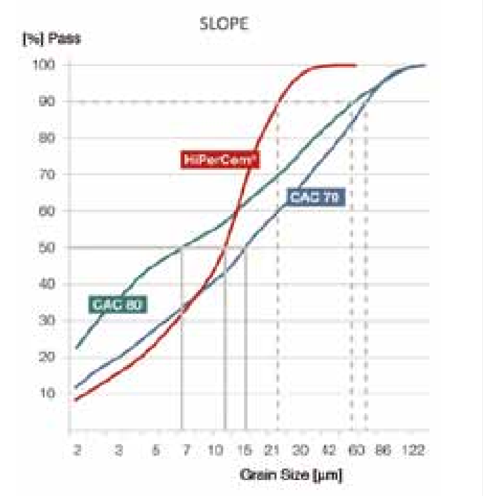


Fig. 3 PSD/slope of CAC vs. HPC

Tab. 1 Process of formulation with the monocalcium aluminate CAC binder HPC

A	CAC 70-content [%]	2,5	5,0	7,5	10,0	15,0
B	CaO [%]	0,7	1,5	2,2	3,0	4,4
C	CA [%]	1,5	2,9	4,4	5,8	8,7
D	**HPC-content [%]**	**1,5**	**3,1**	**4,6**	**6,1**	**9,2**
	Diff. in HPC [%]	*–1*	*–1,9*	*–2,9*	*–3,9*	*–5,2*
E	CaO [%]	0,5	1,0	1,6	2,1	3,1
F	Diff. in CaO [%]	*–0,2*	*–0,4*	*–0,7*	*–0,9*	*–1,3*

chance for a more intensive reaction with the cement.

This paper focuses on a newly developed type of CAC, which offers mainly the reactive hydraulic phase monocalcium aluminate (CA). The chemical composition is close to that of pure CA, so that the existence of other phases such as CA_2 and especially $C_{12}A_7$ is reduced to a minimum. The new concept allows and requires a new approach to the formulation of castables. The CAC content is not used as the guiding parameter, but rather the amount of monocalcium aluminate available. This leads to a higher flexibility for the refractory designer of castables.

2 The new formulation logic

The example (Tab. 1) explains the process of formulation with the monocalcium aluminate CAC binder HPC. Starting with the traditional amount of a standard CAC 70 (line A), the level of CaO is fixed according to line B. As a consequence, this amount of CAC delivers the level of monocalcium aluminate shown in line C.

Taking this line as the basis for the calculation of the amount of HPC, the equivalent amount of HPC is approximately 40 % less than with the use of a standard CAC 70 (line D).

Simultaneously the amount of CaO, which is in most cases an undesired but necessary element, is also reduced (line E), which is summed up in line F. So with the same reactivity, the castable can be designed to a purer state than with the standard CAC 70's. The same process can be applied for CAC 80 with the adjusted values for CA and CaO content.

Of course, the difference between CAC 70 and HPC (indicated under line D in the frame) has to be compensated with the other components of the binder system, such as microsilica or alumina. So either the technical performance can be improved going into purer binder components or the cost can be improved by using cheaper fine aggregates.

3 Setting characteristics

In a standard test formulation, different CAC were tested against the HPC monocalcium aluminate. The general composition of the test mix is:

- 20 % CAC/HPC
- 80 % tabular alumina with PSD 0–3 mm
- 10 % water for all mixes.

In addition to the flow, the evolution of the cold crushing strength after 6–24 h and after drying was also determined. Also, the evolution of the hydration heat was measured to compare it with the physical properties. In two test series HPC was compared with two CAC 70 and 80 selected at random.

Fig. 4–5 show the results of the CAC 70 comparisons. Although especially with type CAC 70 C, the difference in the heat evolution is not very significant, the results of the strength evolution are much different. Whereas the HPC sample, with the pure CA generates after 6 h a CCS of 16 MPa, the other samples with a distinct amount of CA_2, show the same strength level only after 24 h.

Comparing the CAC 80, the difference is much more evident. Both CAC 80's have not developed a measurable strength after 6 h and even after 24 h the strength level is far below that of HPC. This is confirmed by the heat evolution during hydration. HPC develops after approx. 6 h its maximum, whereas the CAC 80 reach their maximum only after approx 11 h and they remain at a far lower level with 27 °C vs. 42 °C for HPC.

4 Comparison of HPC with different CAC in a tabular alumina mix

In order to evaluate the formulation in a high end product, a comparison was made in a tabular mix according to Tab. 2. The formulation shown shall only illustrate the functionality of the HPC cement and not represent a "real world mix", which could surely be improved. The principle of the formulation already explained before can be seen in the blue coloured lines CA and CaO content. The standard is made with a typical regular cement formulation, which is chosen as basis for the CA content.

Replacing the CAC 80 through a CAC 70 leads to only 15 % cement content, where the difference has been replaced through a mixture of reactive and calcined Alumina. To obtain a better rheology, 1,5 % of a superground alumina was added. These types of castables need a deflocculant, which is kept for all other formulations the same to have a better comparison. In the next steps, HPC was introduced on the same CA level (#3) and then stepwise reduced in order to

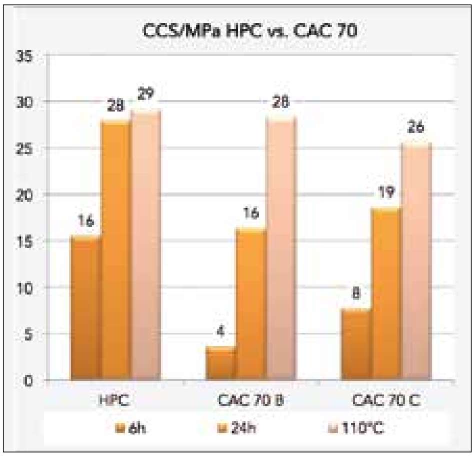


Fig. 4 CCS HPC_CAC 70 early strength

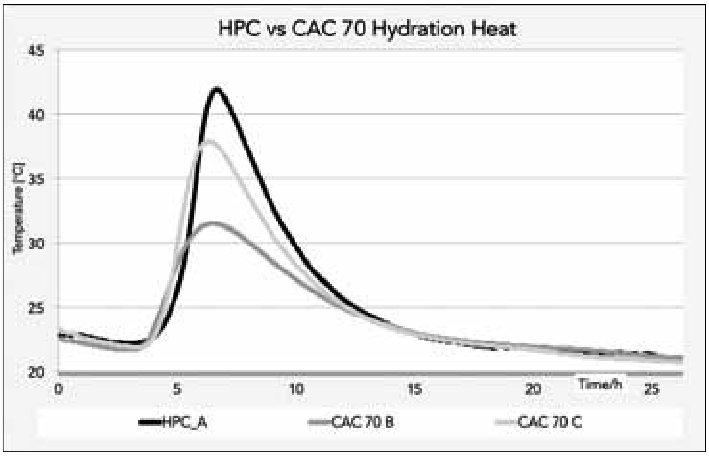


Fig. 5 HPC_CAC 70 exo tests

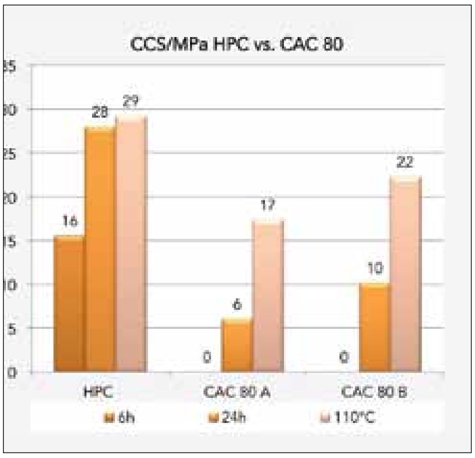


Fig. 6 CCS HPC_CAC 80 early strength

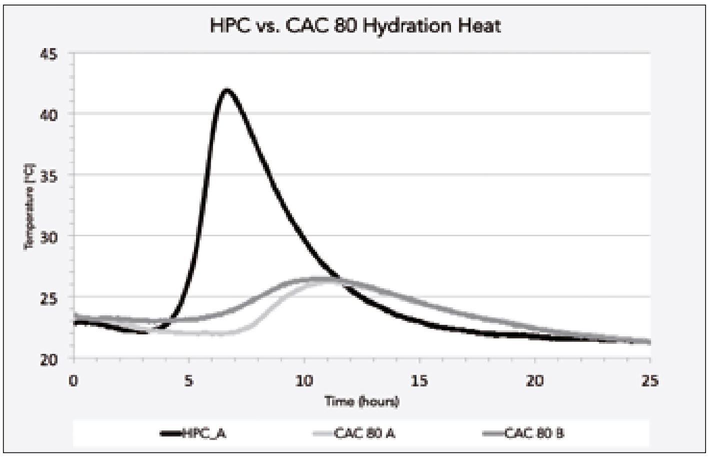


Fig. 7 HPC_CAC 80 exo tests

Tab. 2 Formulations of tabular LCC

	#1/1	#2	#3	#4	#5
	CAC 80 B	**CAC 70 A**	**HPC/9**	**HPC/4,5/1**	**HPC/2,5/1**
Blaine	8100	4120	4510	4510	4510
n	0,5	0,71	1,10	1,10	1,10
HPC [%]			9,0	4,5	2,5
CAC 80 B [%]	25,0				
CAC 70 A [%]		15,0			
CA content [%]	8,8	8,7	8,6	4,3	2,4
CaO content [%]	4,8	4,4	3,1	1,5	0,9
Cast. FS 60 [%]		0,1	0,1	0,1	0,1
ReaAl [%]		1,5	2,5	4,0	4,0
CaAl [%]		2,5	7,5	10,5	12,5
ALC-SG [%]		1,5	1,5	1,5	1,5
TabAl 0–6 mm [%]	75,0	79,5	79,5	79,5	79,5
TabAl 45 µm [%]		4,0	4,0	4,0	4,0
TabAl 0–0,5 [%]	17,5	17,5	17,5	17,5	17,5
TabAl 0,5–1 [%]					
TabAl 0–1 [%]	17,5	18,0	18,0	18,0	18,0
TabAl 1–3 [%]	20,0	19,0	19,0	19,0	19,0
TabAl 3–6 [%]	20,0	21,0	21,0	21,0	21,0
Total	100	100	100	100	100
[%]	8,5	5,9	5,5	5,1	4,8

evaluate the influence of a reduced binder and thus CaO content.

The water addition was added for an initial target flow of approx. 230 mm.

The flow development in Tab. 3, underlines the differences between the HPC and the CAC's. The CAC 80 needs the highest amount of water for the target flow, but it starts very fast to react, which makes it impossible to measure flow after 30 min. The CAC 70 needs less water, also due to the interaction of the admixture and the aluminas. However, an "after fluidification" can be observed.

When HPC is used at an equivalent CA content, the flow is much better, but there is as well a reaction of setting starting after 15 min. Nevertheless the residual flow should allow a proper placement and installation. With further reduction of HPC down to 2,5 % in the mix, the water requirement is also reduced going together with an appropriate flow evolution and an excellent working time as a low flow decay.

Tab. 4 shows the results of the strength measurements. The following conclusions can be drawn:

- Green strength after 24 h is different for all mixes, but on very sufficient level for proper handling.
- The mixes 1/1 to 3 with the same CA level show a straight increase from CAC 80 B to CAC 70 A and HPC
- The strength evolution shows a peak after approx. 1000 °C and with the higher firing temperature a drop.
- Lowering the CA level (mixes 4 and 5) results in a lower but still very sufficient strength level after 24 h and drying but then a continuously increasing sintered strength.
- Mix 4 with only 4,5 % HPC has a higher CCS after 1300 °C than CAC 70 A and compared to CAC 80 B nearly double the strength.
- Obviously, the higher CA content contributes to a high CA_6 formation starting at that temperature.

This is confirmed with the permanent linear change. Whereas the high CA mixes show a strong expansion from 1000 °C to 1300 °C, in the mixes with low HPC content and increasing Alumina addition, the length changes are very moderate, going close to 0 % for Mix HPC 2,5/1 (Fig. 8).

This confirms the low disturbance of the castable texture through CA_6 formation.

To complete the view on the most important parameters, the H.M.O.R. was determined at 1500 °C after 3 h soaking at the same temperature (Fig. 9). Although HPC/9 has the same CA content as the CAC 80 B and CAC 70 A mix, it reveals the highest H.M.O.R. of the whole test series and this in spite of a CaO content approx.1.

Even with only 1/3 of the cement content mix HPC 4,5/1 has a slightly higher M.O.R. than the CAC 70 A mix and only 2,5 % of HPC is sufficient to come to the same level than the CAC 80 B mix with 25 % of cement.

Tab. 3 Flow of tabular mixes

	CAC 80 B	CAC 70 A	HPC/9	HPC/4,5/1	HPC/2,5/1
	8,5 %	**5,9 %**	**5,5 %**	**5,1 %**	**4,8 %**
5 min	231	247	260	261	241
15 min	138	275	262	259	240
30 min	0	262	209	246	231
D Flow [%]	–100	6	–20	–6	–4

Tab. 4 M.O.R. and CCS [MPa]

		CAC 80 B	CAC 70 A	HPC/9	HPC/4,5/1	HPC/2,5/1
		8,5 %	**5,9 %**	**5,5 %**	**5,1 %**	**4,8 %**
M.O.R. **CCS**	**24 h**	4,6	10,0	8,8	5,5	3,0
	110 °C	10,7	19,7	21,1	13,2	7,3
	1000 °C	8,6	15,7	19,6	11,5	7,1
	1300 °C	8,0	10,6	13,3	17,3	14,2
M.O.R. **CCS**	**24 h**	37	112	87	52	26
	110 °C	76	175	172	96	51
	1000 °C	61	147	156	92	64
	1300 °C	75	121	139	139	107

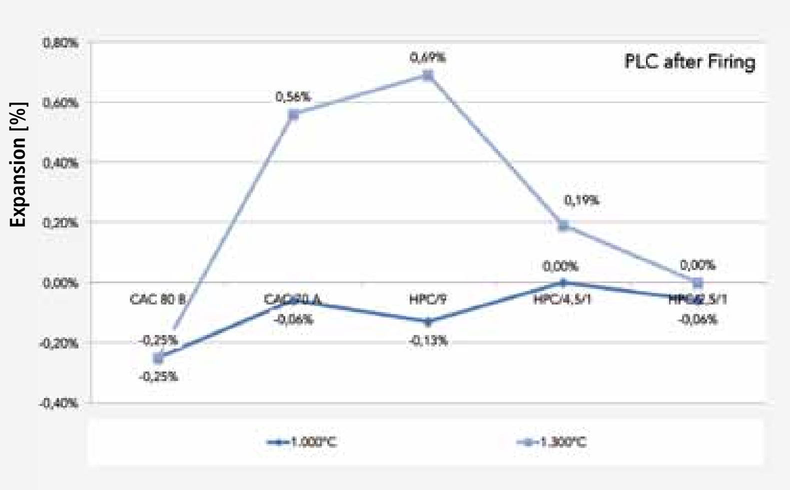


Fig. 8 Expansion of CA mixes [MPa]

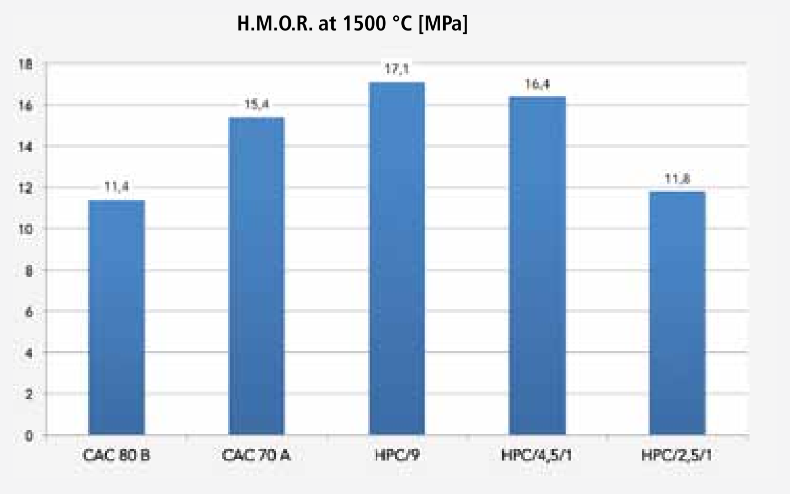


Fig. 9 H.M.O.R. at 1500 °C [MPa]

5 Conclusion for the tabular alumina test series

Adapting a standard mix formulation with HPC to the same CA content leads to a better flow and workability. The strength evolution of M.O.R. and CCS at low and high temperatures shows a favourable benefit of HPC.

Tab. 5 Bauxite: LCC formulations

		BA 70 B	BA HPC 1	BA HPC 2	BA HPC 3	BA HPC 3/1
Binder phase [%]	HPC		2,0	2,0	2,0	2,0
	CAC 70 B	6,0				
	CA content CaO content	3,1 17	1,9 0,7	1,9 0,7	1,9 0,7	1,9 0,7
Binders [%]	MS 955 U GKE MF	4,0 10,0	4,0 14,0	4,0 8,0	4,0 8,0	4,0 8,0
Aggregates [%]	Bauxite <0,09	15,0	15,0	19,0	19,0	19,0
	Bauxite 0–1	10,0	10,0	12,0	6,0	6,0
	Bauxite 1–3	12,0	12,0	12,0	6,0	6,0
	Bauxite 3–6	33,0	33,0	33,0	16,5	16,5
	Bauxite Reg. 0–1				6,0	6,0
	Bauxite Reg. 1–3				6,0	6,0
	Bauxite Reg. 3–6				16,5	16,5
	Durandal 0–1	10,0	10,0	10,0	10,0	10,1
	Total	100,0	100,0	100,0	100,0	100,0
Admixtures [%]	B 4 H	0,10	0,10	0,10	0,10	0,10
Water addition [%]		6,0	6,0	6,0	6,0	6,3
Flow [mm]	5 min	215	220	227	196	217
	15 min	212	215	226	192	212
	30 min	203	214	217	190	201
	∆ Flow	–6	–3	–4	–3	–7

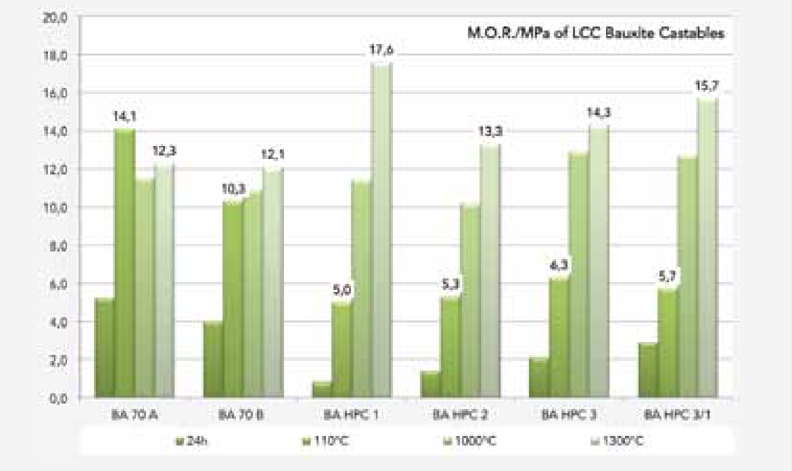


Fig. 10 M.O.R. of bauxite castables

When the CA is lowered down to 2,4 % CA equivalent to 2,5 % of HPC, the balance with the appropriate aluminas can better improve the rheology, without losing the physical properties. When the formulations are redesigned according to this aspect, the permanent linear change can be influenced very positively, as an excessive CA_6 formation doesn't take place, which does not disturb the texture of the castable.

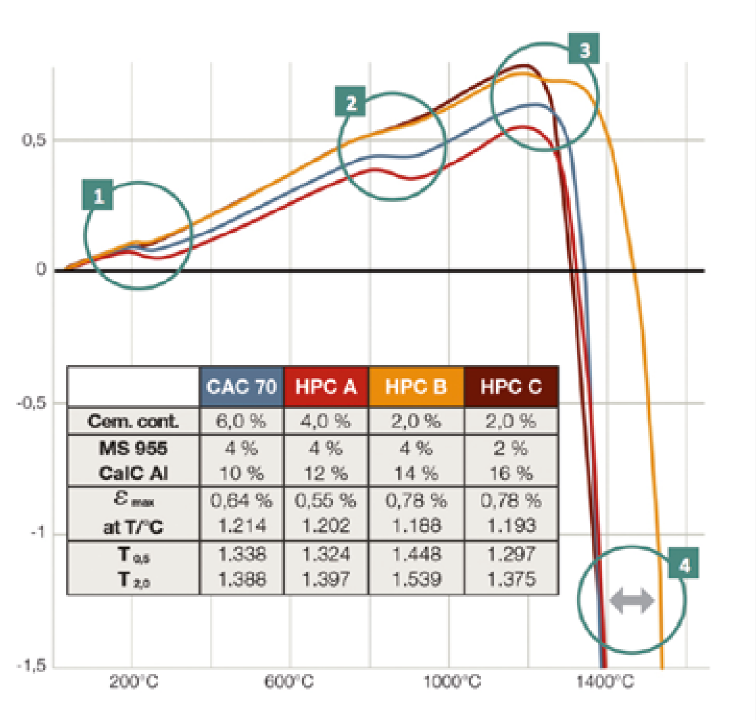
A further highlight is H.M.O.R., here determined at 1500 °C. In spite of lower cement content, the H.M.O.R. is distinctively increased against the standard formulations. Even with the low CA content and thus low HPC, the H.M.O.R. remains at a high level superior or similar to the reference mixes. These results have to be correlated in addition to the definitively lower CaO content. Although this aspect was not investigated in that study it can be assumed, that in combination with excellent physical properties the performance is also improved with respect to slag attack and corrosion resistance, as less CaO is available for reacting to low melting feldspar type minerals.

6 Low cement castables based on bauxite

In a second test series based on bauxite aggregates an evaluation was made, whether it is possible to compensate the reduction of HiPerCem not only with alumina fines but also bauxite fines in order to reduce formulation cost without losing physical properties (BA HPC 2). Moreover, it was checked whether it was possible to replace part of the virgin bauxite with a recycled material BA HPC 3 and 3/1. The latter was added in order to adjust the flow properties with a higher water content. For better comparison the admixture, a HM phosphate with a pH of 4 has been used.

The formulation logic is the same as with the tabular test series regarding the CA and CaO content (see the blue lines). As can be seen from Tab. 5 the flow is not affected when the cement is changed. In mix BA HPC 2, a part of the calcined alumina has been replaced by bauxite fines. The flow is slightly better without any impact on the workability. Going further and replacing 28,5 % of the bauxite with the recycled material, the flow is decreased, but the mix shows no premature setting.

For the physical properties only the modulus of rupture is shown in Fig. 10. As in the previous test series, the same evolution is found with the bauxite aggregates. Replacing the CAC 70 B with HPC, the green strength is lower, but the dried and fired strengths increase dramatically. When replacing in addition part of the alumina with only bauxite fines the strength de-



	CAC 70	HPC A	HPC B	HPC C
Cem. cont.	6,0 %	4,0 %	2,0 %	2,0 %
MS 955	4 %	4 %	4 %	2 %
CalC Al	10 %	12 %	14 %	16 %
ε_{max}	0,64 %	0,55 %	0,78 %	0,78 %
at T/°C	1.214	1.202	1.188	1.193
$T_{0,5}$	1.338	1.324	1.448	1.297
$T_{2,0}$	1.388	1.397	1.539	1.375

Fig. 11 Refractoriness under load

creases but is still above the reference mix. Even when adding the recycled Bauxite the strength is not negatively affected. Surprisingly the increased water addition for better flow has no, resp. little influence of the M.O.R.

Looking to the hot properties (Fig. 11), here refractoriness under load (RuL) shows, that with this formulation design the hot properties can also be improved. When the 6 % of standard CAC 70 is replaced with 2 % HiPerCem and 14 % calcined alumina the behaviour of the formulation is distinctively changed. The four important changes can be listed as:

- The shrinkage due to dehydration is higher with the high cement mixes.
- The transition area when first crystalline phases are formed is also linked with a higher shrinkage for the cement rich compositions.
- The area of mullite formation, where mix HPC B generates obviously much more mullite due to a higher Al_2O_3/SiO_2 ratio than with the others, where CaO is higher.
- This leads to a temperature T_2 (with 2 % shrinkage) of 150 °C higher than with the other formulations.

7 Summary and conclusion

A new type of calcium aluminate cement is presented, which consists nearly completely out of monocalcium aluminate. Moreover the particle size distribution is much steeper, expressed by a higher slope of $n = 1,1$, for better rheology and reactivity of the other elements of the binder system in formulated castables.

This new cement requires a new formulation logic, which focuses only on the content of the reactive monocalcium aluminate and not on the cement content. Thus, it is possible to formulate a reactive binder phase, lowering in parallel the amount of CaO, which is in most cases detrimental to refractory properties as lower refractoriness and sensitivity to slag attack.

It was shown that in a standard quality testing mix, that the new cement has a much faster reactivity and higher green strength than the standard offers. It can be concluded, that CA_2 does not contribute to the hydraulic reactivity in the timeframe, which is important for the placing of refractory castables.

In a test series based on tabular alumina, the new formulation was demonstrated, where the cement content was reduced from 25 % as regular castable down to 2,5 % of HiPerCem with improved properties, starting from flow and working time to physical properties. The expansion due to CA_6 could be nearly completely suppressed, which leads to lower stresses in the refractory lining. Also very surprising, that the hot properties, expressed here as hot modulus of rupture show also strong advantages for the monocalcium aluminate cement.

Similar results were shown in bauxite castables with microsilica, where the same phenomena could be shown. It is also possible to increase the part of bauxite fines without decreasing the mechanical properties, thus enabling also a cost optimization. The refractoriness under load is distinctively improved based on a pure mullite bond, which is not possible with the standard solutions due to their higher CaO content. Next steps of the development will be the evaluation of slag resistance at elevated temperatures with reduced CaO content, but still with good physical properties especially high temperature strengths.

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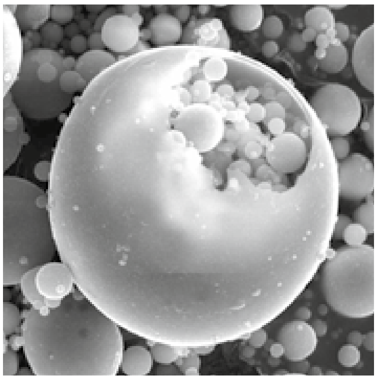

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