Aggregates for Non-ferrous Applications

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In a refractory castable structure coarse grains or aggregates are typically bonded only by physical forces if the application temperature doesn't exceed 1100 °C. In many non-ferrous production processes the castables don't reach sintering temperatures that could support the bonding forces. Due to the thermal expansion mismatch between the aggregates and the matrix, microcrack formation is often the consequence. This weakens the bond between aggregate and matrix. This study demonstrates that calcium aluminate aggregates (CAA) are able to overcome that weakness. They build a strong physical and chemical linkage with much higher bonding forces between CAA and calcium aluminate cement (CAC). This effect is demonstrated here through two examples with two different CAA, a fused pore-free aggregate (R50) and a porous sintered CAA (R60). With R50 mechanical abrasion resistance and as well aluminium penetration resistance have been found superior to bauxite, with less castable required per 1 m^3. R60 enables slightly lower castable density than fireclay and employs at the same time 50 % more open porosity. Despite this difference the flexural strength remains unchanged. This demonstrates that the bonding between CAA and CAC is much stronger than between aggregates from the alumina-silica system and CAC. Both, R50 and R60 are calcium aluminate aggregates which suit applications up to 1350 to 1400 °C for example in power plants, secondary aluminium industry, re-heating furnaces and back-up linings in many industrial furnaces.

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1 Introduction

China is one of the very few countries with very important geological reserves for refractory grade bauxite [1]. Just ten years ago a large amount of this bauxite was available for the global refractory industry at low prices. But now China needs a large portion of this bauxite for its own booming aluminium and steel production. The raw materials industry needs to develop strategies to adjust to the dramatically changed global situation and has the chance to turn it into new opportunities. An example for the use of new calcium aluminate 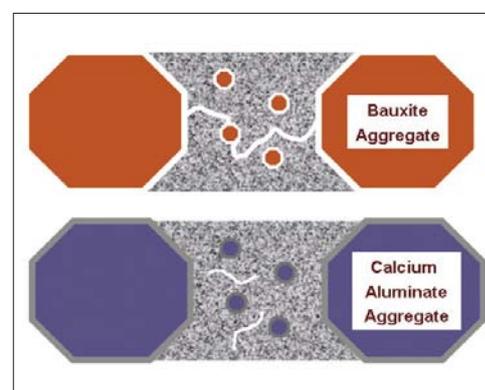aggregate based products was given by [2] which proposed calcium aluminate aggregates for tin bath bottom bricks to overcome problems with alkalis when aggregates from the alumina-silica systems are used. Other publications discussed the application of calcium aluminate aggregates in bricks [3] and castables [4, 5] for the non-ferrous and other industries. This present study specifically highlights the bonding mechanism between calcium aluminate aggregates and the calcium aluminate cement matrix. This unique bonding system results in very specific properties that are of advantage for non-ferrous applications. Those calcium aluminate aggregates that are consisting of hydraulic phases like CA and CA_2 have the potential to interact chemically on the surface with the calcium aluminate binder, unlike aggregates which consist of corundum, mullite, or CA_6 (Fig. 1). This stronger bonding effect and its impact on physical properties will be investigated in this paper in comparison to bauxite and fireclay.

2 Calcium aluminate aggregates

Calcium aluminate cement is known for many years as binder for refractory castables. Also, calcium aluminate aggregates are known from peri-refractory applications (ALAG®) and from application as fluxing material for metallurgical slag (LDSF®). Both are fused materials and start to melt below

Fig. 1 Reaction zone on CAA surface connects aggregates closely with the CAC matrix unlike with bauxite where microcracks surround the aggregate

Tab. 1 Chemistry and mineralogy of aggregates

		Surface reactive aggregates			Inert aggregates	
		Calcium aluminates			Fireclay	Bauxite
		R60	R50	ALAG®	LDSF®	FC	BX
		sintered	fused	fused	fused	sintered	sintered
Al_2O_3		62	52,5	39,5	41	45,6	89,5
SiO_2		6	5,5	4,5	3,5	51,5	4
CaO		26	37	37,5	50,5	0	0,1
Fe_2O_3		2,5	2	15,5	2	0,9	1,5
TiO_2		2,5	2	2	2	1,7	3,7
		99	99	99	99	99,7	98,8
Main phase		CA_2	CA	CA	$C_{12}A_7$	A_3S_2	A
Grain BD [g/cm³]		2,2	2,9	3,2	2,7	2,5	3,2
Porosity [vol.-%]		30	1	1	1	4	4

Tab. 2 Model regular castable recipes CC-R50 and CC-BX

	Fraction [mm]	Unit	CC-R50	CC-BX
R50	3−5	[%]	31	-
R50	1−3	[%]	20	-
R50	0−1	[%]	29	-
Bauxite	3−6	[%]	-	31
Bauxite	1−3	[%]	-	20
Bauxite	0−1	[%]	-	29
Secar® 51		[%]	20	20
H_2O		[%]	9,7	9,7
Working time		[min]	240	240

1400 °C, ALAG® due to its relatively high iron oxide content combined in different aluminate phases, and LDSF® due to its high $C_{12}A_7$ mineral phase content (Tab. 1). ALAG® is for example used in the back-up zones of blast furnace cast houses and the blast furnace slag granulation station. Other fields of application are the ramps in coke oven plants or industrial floors in the aluminium industry where high abrasion resistance is required but at ambient or relatively low furnace temperature. R50, a low-iron oxide, fused calcium aluminate aggregate

Fig. 2 R50 aggregates (fraction 3 − 5, 1 − 3 and 0 − 1 mm)

has been presented by [4]. Compared to ALAG® the R50 product contains more Al_2O_3 and much less Fe_2O_3 which makes it suitable for non-ferrous application fields. This pore-free aggregate has a high content of calcium mono-aluminate (CA) and a low amount of $C_{12}A_7$ phases. Fig. 2 shows the three fractions of R50 that have been used in this study. Fig. 2 R50 aggregates (fraction 3−5, 1−3 and 0−1 mm). The fused, pore-free aggregate R50 has been compared with bauxite in order to investigate the potential as aggregate in areas where high abrasion resistance, low non-ferrous metal penetration and/or low accretion formation is required like in DRI. Furthermore R60, a sintered and quite porous calcium aluminate aggregate with more than 60 % Al_2O_3 and calcium di-aluminate (CA_2) as main phase has been investigated. Objective was to verify if even a CA_2 based aggregate would improve bonding forces since CA_2 has a lower hydraulic reactivi-

ty than CA. The porous R60 has been compared with dense fireclay in order to study its ability to reduce castable density without penalising on strength. Objective is to improve heat containment in furnaces and to save energy.

3 Test methods

Different model castable systems have been chosen to investigate the bonding reaction between the calcium aluminate cement and the aggregates. Regular castables (Tab. 2, 4) as well as deflocculated medium cement castables (MCC) have been investigated (Tab. 3). Classical castable test methods as vibration flow, porosity by water immersion and strength measurements have been used to study the basic castable properties. Quantitative chemical and mineralogical analyses have been conducted using the XRF and XRD methods. The scanning electron microscopy has been used to investigate the microstructure and surface reactions on the calcium aluminate aggregates. The refractoriness under load method was used to verify the hot properties of the aggregates. Abrasion tests according to ASTM C 704 have been conducted and as well corrosion tests with aluminium alloys in crucibles.

4 Test results
4.1 Calcium aluminate aggregate R50 in regular castable

R50 has been employed in a conventional regular castable replacing Chinese bauxite (Tab. 2). As can be seen in Fig. 3 both castables exhibit a very similar flow profile with the same amount of mixing water. The reactive calcium aluminate phases on the surface of R50 don't disturb the rheology. Working time is equal to the bauxite based castable. But compared to bauxite the R50 reduces the castable density by 10 % (Fig. 4). Despite the lower density the cold modulus of rupture increases by almost 30−50 % after firing at 800 and 1200 °C (Fig. 5). The refractoriness under load test indicates that the bauxite mix starts to soften at lower temperatures than R50 but then keeps its form up to higher temperatures so that the maximum application temperature for the CC-R50 mix would be in the range of 1350 °C and for CC-BX about 1400 °C (Fig. 6).

The castable surface after the ASTM C-704 abrasion test is shown in Fig. 7. In case of bauxite the matrix is more eroded and the bond between bauxite and cement matrix is
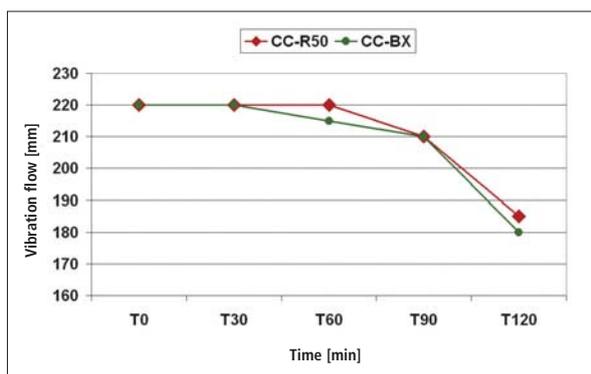
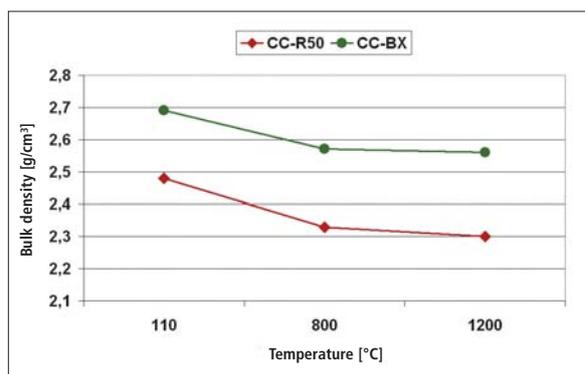**Fig. 3** Vibration flow of regular castables CC-R50 and CC-BX at 20 °C

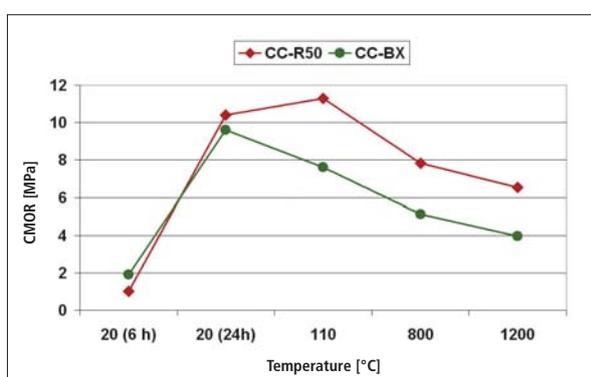**Fig. 4** Bulk density of regular castables CC-R50 and CC-BX

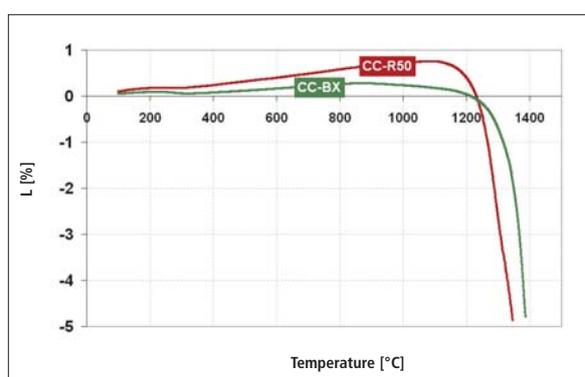**Fig. 5** CMOR of regular castables CC-R50 and CC-BX

Fig. 6 Refractoriness under load (0,2 MPa) of regular castables CC-R50 and CC-BX

significantly weakened. In case of R50, the aggregate and matrix remain bonded together which results in a more homogeneously erosion and a significantly reduced material loss. An abrasion repeatability test with 10 separately produced samples of both castables resulted in average in an eroded volume of 11 cm³ for CC-BX and less than 8 cm³ for CC-R50 (Fig. 8). This is an extraordinary good result for a conventional castable. This low value can typically only be achieved with alumina-silica aggregates when much more sophisticated castables are used employing fillers and deflocculants into the system [6]. This makes these castables more sensitive to castable installation conditions. R50 enables excellent abrasion resistance even with very robust formulation concepts.

The reason for this excellent behaviour of R50 can be found in the microstructure (Fig. 9). Around the R50 grains a reaction layer occurs which provides an intimate contact between the grain and the matrix. Furthermore and unlike in case of bauxite very few microcracks occur around the grains.

In Fig. 10 it becomes obvious that the reaction layer creates the strong bond between

Tab. 3 Model MCC with bauxite (B1–B3) and R50 (R1–R3) with different barium sulphate powder contents

	Unit	Bauxite			R50		
		B1	B2	B3	R1	R2	R3
R50 3–5 mm	[%]	-			33		
R50 1–3 mm	[%]	-			12		
R50 0–1 mm	[%]	-			20		
Secar® 51	[%]	-			-	5	5
Bauxite 3–6 mm	[%]	21			-		
Bauxite 1–3 mm	[%]	22			-		
Bauxite 0–1 mm	[%]	22			-		
Bauxite 0–0,09	[%]	-	5	5	-		
Calcinated alumina	[%]	-	-	5	-	-	5
BaSO$_4$	[%]	10	5	-	10	5	-
Reactive alumina	[%]	10			10		
Secar® 71	[%]	15			15		
PP fibres	[%]	0,05			0,05		
Peramin® AL 200	[%]	0,15			0,12		
H$_2$O	[%]	5			4,5		

the matrix and the aggregate which results in a kind of continuum between the grain and the matrix due to the same mineralogy and chemistry of matrix and aggregate.

4.2 R50 in deflocculated medium cement castable (MCC)

The effect of R50 in a model MCC recipe (Tab. 3) with 15 % Secar® 71 and different contents of barium sulphate as aluminium anti-wetting material is discussed below. While for a bauxite castable barium sulphate is necessary to get the required anti-wetting effect the amount can be reduced or even completely eliminated when R50 is used to increase the maximal possible service temperature [5].

A microsilica-free MCC with Secar® 71 as binder has been chosen to minimise potential reactions between the aluminium melt and the castable matrix. A polycarboxylate ether (Peramin® AL 200) has been used to deflocculate the mixes very efficiently. By replacing

bauxite with R50 water addition and deflocculant addition could be reduced and still a better fluidity could be achieved (Fig. 11). Open porosity after heating at 800 and 1200 °C, the critical temperature range for the aluminium application, is in all cases significantly lower with R50 despite a lower bulk density (Figs. 12, 13). Irrespectively of the $BaSO_4$ content a high crushing strength level has been found with R50 (Fig. 14). If an unexpected overheating in an aluminium furnace would occur, here simulated by a pre-firing at 1400 °C, then R50 would secure much better volume stability than bauxite (Fig. 15). Furthermore porosity remains on a low level so that the risk of aluminium penetration remains low even after deterioration of barium sulphate due to its limited thermal stability. In Fig. 16 results from aluminium cup tests at 800 °C/72 h are shown. While no penetration occurs neither with bauxite nor with R50 when 10 % barium sulphate are in the recipe, penetration commences when bauxite is used with-

out addition of barium sulphate. R50 prevents aluminium penetration even when the mix is free of $BaSO_4$.

4.3 Calcium aluminate aggregate R60 in regular castable

The R60 aggregate is a sintered calcium aluminate grain with about 30 % open porosity, much higher than for the fireclay which has been used here as a reference (Tab. 1). A conventional castable model recipe (Tab. 4) has been used to compare the rheology of the fireclay-based castable CC-FC with the R60-based CC-R60. Both need the same amount of water to reach identical initial flow properties. While fluidity under vibration slightly increases during the first 30 min, it then remains almost stable when fireclay is used (Fig. 17). The higher flow decay in the case of R60 is due to the higher pore volume into which the water migrates over time. Then less water is available to keep the cement matrix fluid and the castable starts to stiffen.
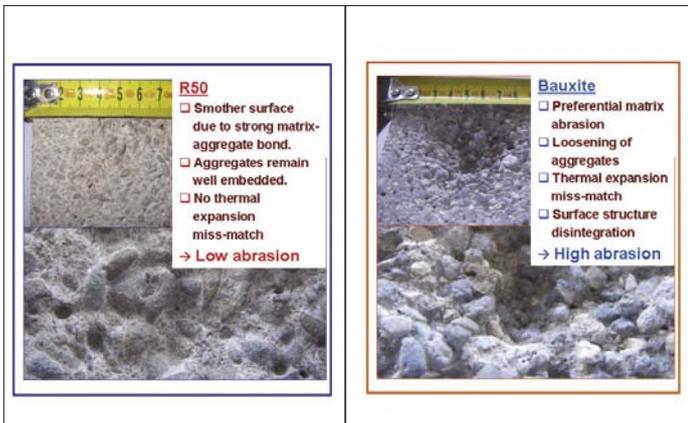

Fig. 7 Regular castable after abrasion test

Fig. 8 Abrasion repeatability test with 10 samples of castable CC-R50 (left) and of castable CC-BX (right)
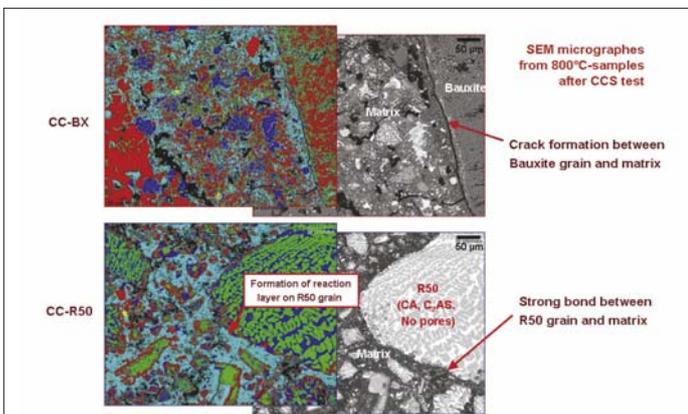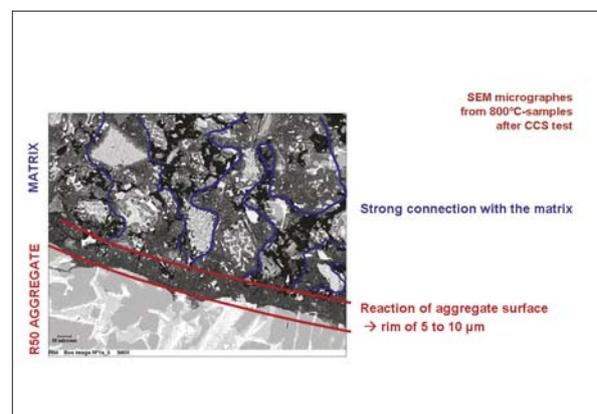

Fig. 9 SEM micrograph of CC-BX and CC-R50 matrix

Fig. 10 SEM micrograph of reaction layer between R50 grain (big light grey grain at bottom) and matrix (dark grey area in upper part)
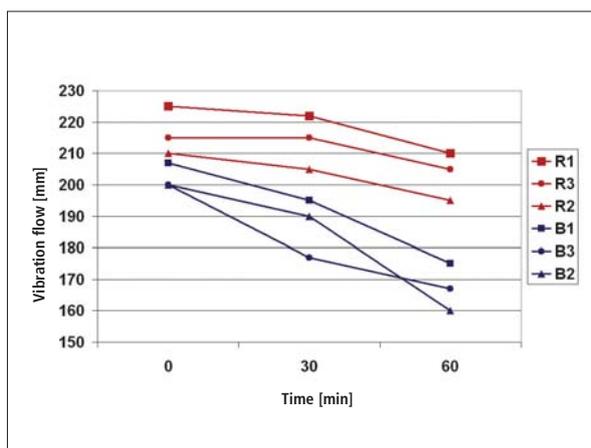
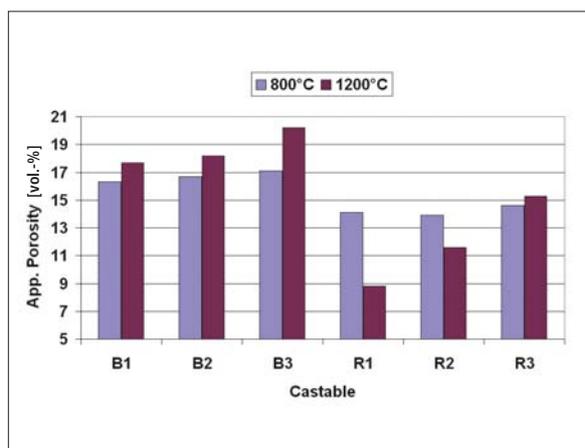**Fig. 11** Flow profile of MCC with R50 (R1–R3) and bauxite (B1–B3)

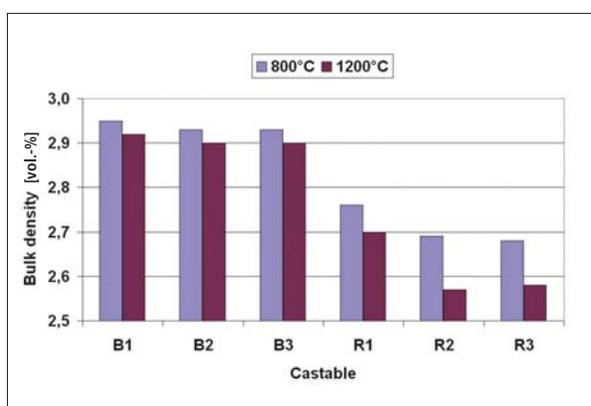**Fig. 12** Apparent porosity of MCC with R50 (R1–R3) and bauxite (B1–B3)

Fig. 13 Bulk density of MCC with R50 (R1–R3) and bauxite (B1–B3)
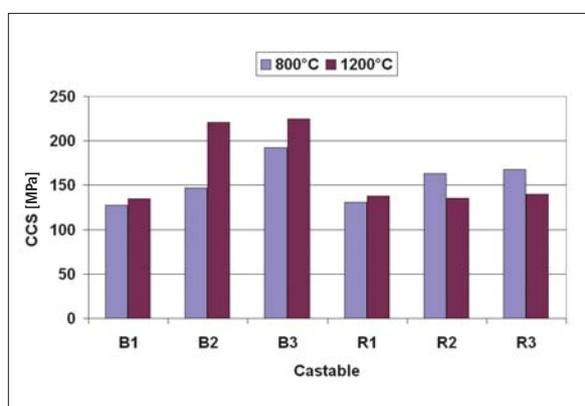

Fig. 14 Cold crushing strength of MCC with R50 (R1–R3) and bauxite (B1–B3)

It is assumed that the drop of flow is not the effect of the mineralogy of R60 since it contains mainly the CA_2-mineral phase which has only little hydraulic properties at 20 °C. The observed stiffening effect with R60 could be an interesting property for gunning mixes but has not been further studied here. After firing at 800, 1100, and 1350 °C the bulk density of CC-R60 is about 5 % lower than CC-FC (Fig. 18) and open porosity is almost 40 % higher (Fig. 19). With classical aggregates from the alumina-silica system one would expect a drop in strength [7]. But in this case, despite the lower bulk density and higher porosity with R60, flexural strength remains similar to CC-FC (Fig. 20).

To calculate the temperature stability of the castable matrix compositions (fraction < 1 mm) the FactSage® software has been used. It shows that solidus and liquidus temperatures of the R60 containing mix are higher than for the fireclay mix despite the mullite content in fireclay (Fig. 21). Here the CA_2 based R60 aggregate

Tab. 4 Model regular castable recipes CC-FC and CC-R60

	Fraction [mm]	Unit	CC-FC	CC-R60
R60	3–6	[%]	-	28
R60	1–3	[%]	-	25
R60	0–1	[%]	-	22
Fireclay	3–6	[%]	28	-
Fireclay	1–3	[%]	25	-
Fireclay	0–1	[%]	22	-
Secar® 51		[%]	25	25
H_2O		[%]	8,5	10,5
Working time		[min]	240	220

combined with calcium aluminate cement shows superior temperature resistance.

5 Summary and conclusion

The calcium aluminate aggregates R50 and R60 show very particular properties due to their specific mineralogical nature which is very similar to the calcium aluminate cement. On the aggregate surface chemical reactions with the cement occur which creates a strong linkage between aggregate

and matrix. A reaction layer forms around the grains to provide a direct linkage to the cement matrix. This unique property makes R50 and R60 especially interesting for refractory castables und gunning mixes for the non-ferrous industry. Both, R50 and R60 calcium aluminate aggregates can be used up to 1350 to 1400 °C depending on the castable type and the used calcium aluminate cement and filler. The fused R50 aggregate has very little open porosity but
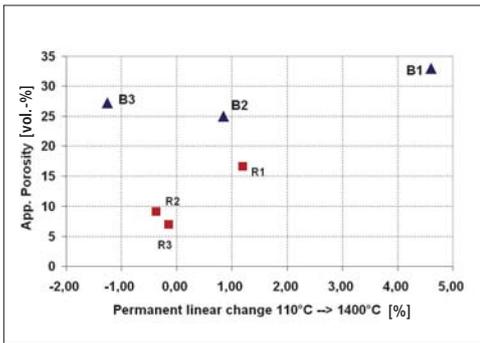
Fig. 15 Permanent linear change and apparent porosity after firing at 1400 °C of MCC with R50 (R1–R3) and with bauxite (B1–B3)
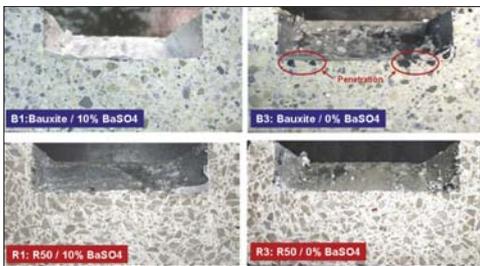

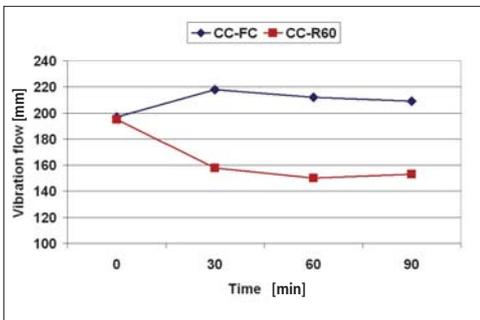**Fig. 16** Aluminium cup tests with alloy 7075 at 800 °C / 72 h

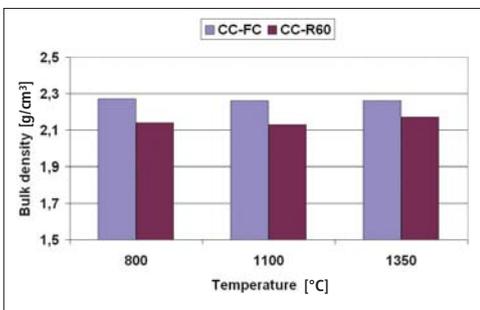**Fig. 17** Vibration flow of regular castables CC-FC and CC-R60 at 20 °C

Fig. 18 Bulk density of regular castables CC-FC and CC-R60

a lower density compared to bauxite due to its calcium aluminate composition. Despite the lower density strength is even higher with R50. A given furnace design for example in power plants can now be lined with less material without penalising on strength. R50 suits particularly applications in areas with high abrasive load and is therefore of high interest for example in power plants.

Significantly better abrasion resistance can be achieved when bauxite is replaced by R50 in conventional but robust castable and gunning mixes. R50 applied in microsilica-free medium cement castable for aluminium applications opens new ways to design mixes with a high penetration resistance to aluminium alloys.

R50 modifies the pore structure towards very low open porosities even after firing at 1400 °C.

Barium sulphate starts to decompose at 1200 °C which leads to a massive volume expansion at 1400 °C when bauxite is used. Volume stability is much better when R50 is employed in the mix. Due to the modified bonding properties and the low wettability of calcium aluminates with aluminium the barium sulphate content can even be reduced or eliminated when R50 is used and helps to give more safety when unforeseen over-heating of a furnace occurs.

The sintered and porous R60 aggregate opens new ways to formulate gunning mixes. Despite the higher castable porosity and lower density compared to dense fireclay, equivalent strength levels are achievable. This makes R60 interesting when better heat containment is required without penalizing for example on flexural strength as for example in back-up linings of furnaces.

References

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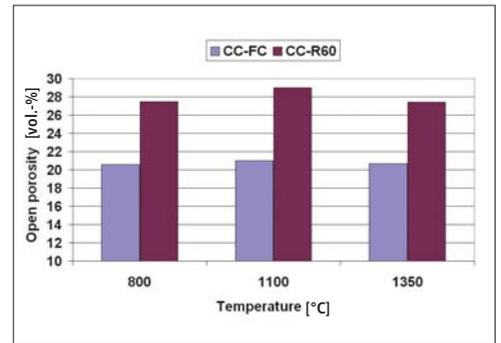
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Fig. 19 Open porosity of regular castables CC-FC and CC-R60

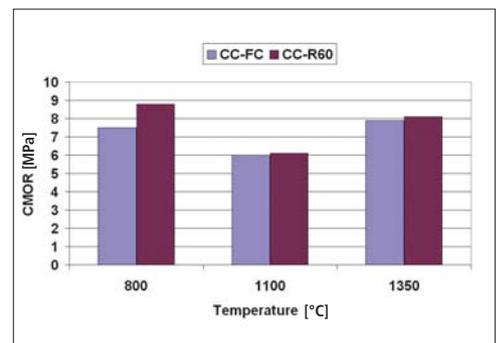**Fig. 20** CMOR of regular castables CC-FC and CC-R60
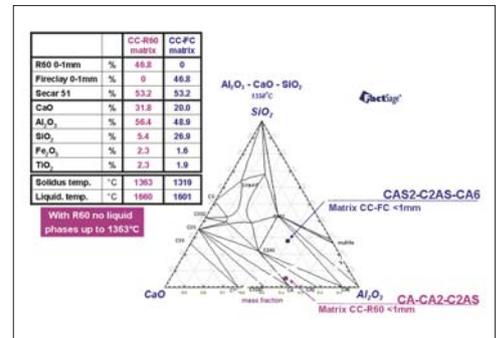
Fig. 21 Solidus and liquidus temperatures for castable matrix (<1 mm)