The Influence of SiO_2 and Spinel on the Hot Properties of High Alumina Low Cement Castables

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Abstract

Different alternatives in improving the hot strength of low cement vibration and self flowing Tabular Alumina castables were investigated. Castables with a CaO content of typically 1.5% were mainly examined. A 70% Al_2O_3 cement was used. Also a new developed 95% Al_2O_3 cement was tested. The influence of additions of microsilica (0.2–2%) and spinel on porosity, the cold and hot strength, refractoriness under load and thermal shock resistance have been studied. Silica in concentration as low as 0.2% degraded hot strength and refractoriness under load substantially. Spinel addition improves hot strength remarkably. As an alternative to cement bonding an alumina bonding system has been evaluated. Only pure cement bonded Tabular Alumina castables show high hot strength up to 1650 °C.

1. Introduction

The existence of low melting phases in the system Al_2O_3-SiO_2-CaO made the reduction of cement to a key technical trend in the last 25 years to improve hot performance of castables. The development of LCC, ULCC and NCC were logical steps in the attempt to reduce the formation of liquid phases at temperatures as low as 1300–1400 °C when silica containing raw materials like bauxite, andalusite, fireclay and mullite are used.

Surprisingly a similar approach has been made with synthetic alumina raw materials like tabular alumina or white fused alumina which contain practically no silica. The use of microsilica as a flow enhancer in synthetic Al_2O_3 castables can be considered as a conscious decision not to use the potential benefits of the pure system Al_2O_3-CaO to its full advantage. Extensive work has been performed until recently [1–3] to discover ways to minimize the negative effects of microsilica additions on the hot strength of cement bonded castables. Undoubtedly cement reduction is the most effective approach to improve hot performance of silica containing raw materials. It is a key question if the same strategy should be used for pure alumina raw materials, especially when taking into account the severe placement consistency problems and low green strength the refractory user is facing when the cement content is reaching very low levels.

This paper investigates different alternatives in improving the hot properties of cement bonded Tabular Alumina castables. Castables with a CaO content of typically 1.5% were mainly used. The selected CaO content assures sufficient green strength in combination with proper placement consistency. The matrix composition avoids the formation of phases which melt below about 1800 °C [4–6]. As cement a 70% Al_2O_3 type (CA-14M) and a new developed 95% Al_2O_3 cement (XAC-95) were used.

Both vibration and selfflowing castables have been tested. The influence of additions of micro-silica (between 0.2 and 2%), MA spinels and casting water on porosity, cold and hot strength, refractoriness under load and thermal shock have been investigated. As an alternative to cement bonding a new pure alumina based binder system (Alphabond) has been evaluated.

2. Raw Materials and Castables

Over 30 compositions of Tabular Alumina based low cement castables were investigated.

The used raw materials are listed in **Tab. 1** and compositions of selected castables are shown in **Tab. 2.** Two base compositions with 5% cement, one suitable for vibration casting, one designed for selfflowing were varied by addition of microsilica, spinel and other bonding systems, one based on a new 95% alumina cement (XAC-95) and one based on a pure alumina bond (Alphabond).

The composition and grain size distribution of the two base mixes are shown in **Tab. 3** and **Fig. 1.**

Tab. 1. Chemical composition of used raw material

%	Tabular alumina T 60	Spinel AR 90	Spinel AR 78	Reactive alumina CL 370 C	Reactive alumina CT 3000 SG	Alphabond 100	70 % Alumina Cement CA-14 M	95 % Alumina Cement XAC-95
Al_2O_3	99.4	89 – 90	76 – 77	99.8	99.8	90	72.7	94 – 95
Na_2O	0.36	<0.17	<0.15	0.06	0.08	0.5	0.19	0.4 – 0.5
CaO	0.05	<0.25	<0.3	0.02	0.02	<0.1	26.5	4.7 – 5.0
MgO	<0.10	9 – 10	22 – 23	0.02	<0.12	n.d.	0.09	0.04
SiO_2	0.02	<0.05	<0.06	0.02	0.02	0.2	0.2	0.05
Fe_2O_3	<0.10	<0.10	<0.10	0.02	0.02	n.d.	0.11	0.03
L.O.I.	÷	÷	÷	÷	÷	9	÷	0.7 – 0.8

Additives

Mikrosilika 971 D:	min. 96 % SiO_2, max. 0.9 % alkaline.	Elkem Refractories
Darvan 7 S:	Sodium salt of a carboxylated polyelectrolyte.	R. T. Vanderbilt Company, Inc.
Tecnos 95 PWD CAS/AC 1:	alkaline/-earth salt of polynaftalene sulphonic acid.	Technochem Italiana S.r.l.

Tab. 2. Compositions of selected castables

Castable No.			1	3	4	5	6	7	8	9	10	11	12	15	18	19	20	21	22	23	24	25	26	27
Tabular Alumina	T-60	> 1 mm	■	■	■	■	■	■	■		■	■	■		■	■	■	■		■	■	■	■	■
		0.045 – 1.0 mm	■	■	■	■	■	■	■		■	■	■		■	■	■	■		■	■	■	■	■
		0 – 0.045 mm																						
		0 – 0.020 mm	■	■	■	■	■					■	■			■	■	■	■	■	■	■	■	■
Spinel	AR 90	> 1 mm									■			■										
		0.045 – 1.0 mm									■			■							■			
		0 – 0.045 mm																						
		0 – 0.020 mm												■										
Spinel	AR 78	> 1 mm								■														
		0.045 – 1.0 mm								■														
		0 – 0.045 mm								■														
		0 – 0.020 mm						■	■	■	■										■			
Reactive Aluminas	CL 370 C		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
	CT 3000 SG																					■		
70 % Alumina Cement	CA-14 M		■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■			
Mikrosilica					■	■	■		■				■									■	■	■
Alphabond 100																						■	■	■
95 % Alumina Cement	XAC-95														■									

Tab. 3. Composition of the basis Tabular Alumina castables (further informations see Tab. 1)

		Vibration type No. 11 [%]	self flow type No. 3 [%]
Tabular Alumina	1/4" – 8 mesh		35
	3 – 6 mesh	26	
	6 – 10 mesh	5	
	8 – 14 mesh	9	10
	14 – 28 mesh	14	10
	28 – 48 mesh	11	5
	48 – 200 mesh	8	5
	−20 µm	10	20
reactive alumina	CL 370 C	12	10
cement	CA 14 M	5	5
dispersants	Darvan 7 S	0.24	0.1
	Tecn. 95 AC 1	0.07	
	H_2O	5	5.7

3. Preparation of Test Pieces by Vibration or Selfflowing Casting and Test Conditions

Preparation of the test specimens followed according DIN 51010 resp. 26 to 28. PRE-Recommendations.

The dry batch is pre-mixed in an intensive mixer (120 rpm) for approx. one minute. After slowly adding the necessary amount of demineralized water a four (vibration castables) or five (selfflowing castables) minute mixing is performed.

The metal moulds are filled and vibrated using an amplitude of 0.60 mm, 50 Hz, 30 sec.

The test pieces are immediately cured at 32 °C/24 h (min. 90 % of relative humidity). The dimensions of the test pieces are measured after demoulding and after drying at 110 °C/24 h. The cured specimens are fired at a heating rate of 6 °C/min., 1000 °C/5 h or 1500 °C/5 h.

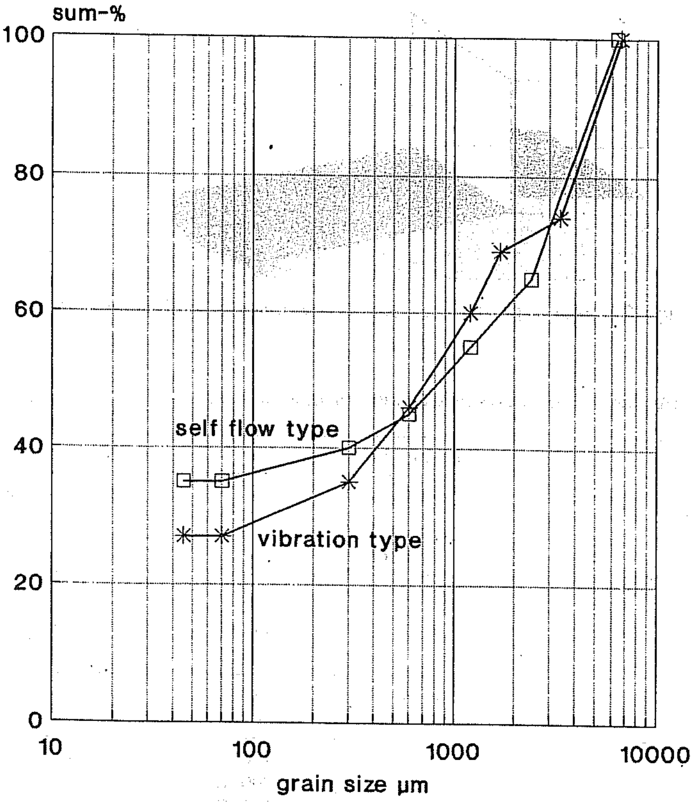

Fig. 1. Grain size distribution of the base Tabular Alumina castables (see also Tab. 3)

Tab. 4 gives an overview of specimen sizes, pretreatment and test methods of the castables.

To determine the water demand of a vibration castable the following procedure was used:

The mix is moulded into Vicat-moulds (7.5 resp. 6.6 cm diameter). Demoulding after 30 min is followed by a vibration for

Tab. 4. Used test specimen sizes, pre-treatment and test methods

specimen size	pre-treatment	measured properties	test method
40 mm × 40 mm × 160 mm	cured 32 °C / 24 h 110 °C / 24 h 1000 °C / 5 h 1500 °C / 5 h	permanent linear change (P.L.C.), cold modulus of rupture (M.O.R.), cold crushing strength (C.C.S.), bulk density, apparent porosity	DIN 51 010 resp. 26.–28. PRE-Recommendation
25 mm × 25 mm × 150 mm	1500 °C / 5 h	hot modulus of rupture (H.M.O.R.)	DIN 51 048, part 1 resp. 18. PRE-Recommendation
54 mm × 64 mm × 230 mm cylinder 35 mm diameter, 35 mm height	110 °C / 24 h 1500 °C / 24 h	refractoriness under load (R.U.L.), thermal shock resistance (water and air quenching), hot crushing strength (H.C.S.) at 1650 °C (selected castables)	DIN 51 053, part 1 resp. ISO 1893, DIN 51 068, part 1 and 2 resp. 5. PRE-Recommendation

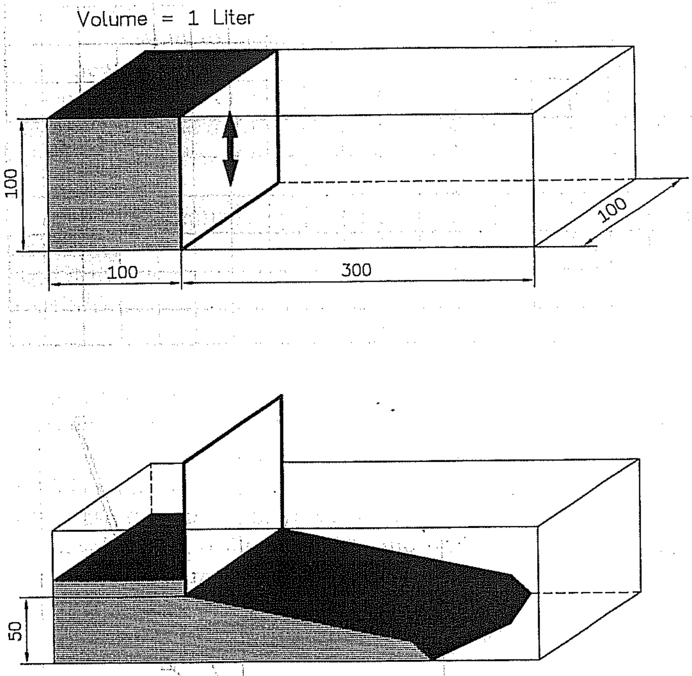

Fig. 2. Test apparatus for testing flowability of selfflowing castables

30 sec. with an amplitude of 0.60 mm. The average diameter the spread mix is measured. Proper consistency is obtained at diameter of 14.7 ± 0.7 mm.

To determine water demand of a selfflowing castable follo ing procedure is used:

One litre of the castable mix is filled in the test apparatus de cribed in **Fig. 2.** Proper water content is reached when, aft opening the slide by 50 mm, the mix reaches the opposite wa after 30 sec.

4. Results

Properties of selected castables are compiled in **Tab. 5 a – c**

4.1 Permanent linear change of dimension (P.L.C.)

The P.L.C. values of all tested castables after drying a firing at 1000 °C range between ± 0.1%.
When firing at 1500 °C the microsilica containing castab (tested up to 2% addition) show shrinkage up to 1.4%. T

Tab. 5a. Properties of low cement Tabular Alumina and spinel vibration castables (main composition see Tab. 2)

Castable No.			11	18	10	9	15
grain			Tabular Alumina	Tabular Alumina	+ AR90 + AR78 spinel	+ AR78 spinel	AR90 spinel
cement bond			CA-14M (5 %)	XAC-95 (40 %)	CA-14M (5 %)	CA-14M (5 %)	CA-14M (5 %
Mixing water %			5	5	4.7	5.6	5.5
bulk density	g/cm³	*110 °C 1500 °C	3.12 3.01	– 3.0	3.11 3.07	2.90 2.84	2.93 2.86
apparent porosity	Vol.%	110 °C 1500 °C	14.0 19.3	– 19	13.2 17.4	14.6 19.3	16.3 22.4
M.O.R.	N/mm²	110 °C 1000 °C 1500 °C	14 15 40	19 13 46	9 8 39	8 6 37	9 9 34
C.C.S.	N/mm²	110 °C 1000 °C 1500 °C	80 90 184	110 89 185	78 78 235	58 55 207	54 43 97
H.M.O.R. at 1500 °C	N/mm²	1500 °C	16	21	21	14	12
R.U.L. T₀₅	°C	1500 °C	1690	>1700			>1700
P.L.C.	%	1500 °C	0	0.1	−0.1	−0.2	−0.1

* pre-treatment temperature

Tab. 5b. Properties of low cement Tabular Alumina and spinel self flowing castables (main composition see Tab. 2)

Castable No.			1	3	7	24
grain			Tabular Alumina	Tabular Alumina	+ fine spinel (20 %)	+ AR90 + AR78 spinel
cement bond			CA-14M (5 %)	CA-14M (5 %)	XAC-95 (40 %)	CA-14M (5 %)
Mixing water %			5	5.7	5.7	5.7
bulk density	g/cm^3	*110 °C 1500 °C	3.16 3.10	3.13 2.98	3.07 2.97	3.09 3.04
apparent porosity	Vol.%	110 °C 1500 °C	13.4 17.4	14.5 20.5	14.4 20.1	13.2 17.7
M.O.R.	N/mm^2	110 °C 1000 °C 1500 °C	12 9 49	10 8 42	9 6 30	16 11 42
C.C.S.	N/mm^2	110 °C 1000 °C 1500 °C	81 59 227	52 47 187	67 63 153	82 59 210
H.M.O.R. at 1500 °C	N/mm^2	1500 °C	13	8	17	22
R.U.L. T.$_{05}$	°C	1500 °C		1660	1680	
P.L.C.	%	1500 °C	0	−0.1	−0.2	0

* pre-treatment temperature

Tab. 5c. Properties of Tabular Alumina and spinel vibration castables with addition of microsilica (main composition see Tab. 2)

Castable No.			12	6	5	4	8	25	26	27
grain			Tabular Alumina	Tabular Alumina			+ AR 78 spinel	Tabular Alumina	Tabular Alumina	Tabular Alumina
bond			CA-14M (5 %) + 0.5 SiO_2	CA-14M (5 %) + 0.2 % SiO_2	+ 0.5 % SiO_2	+ 2 % SiO_2	CA-14M (5 %) + 0.5 % SiO_2	Alphabond SiO_2 (3 %)	Alphabond SiO_2 (3 %)	Alphabond SiO_2 (6 %)
mixing water %			5.0	5.7			5.7	4.3	5.6	5.6
bulk density	g/cm^3	*110 °C 1500 °C	3.13 3.06	3.12 3.07	3.0 3.08	3.09 3.13	3.04 2.90	3.07 3.11	3.08 3.19	– 2.96
apparent porosity	Vol.%	110 °C 1500 °C	13.7 17.7	14.5 18.3	15.2 17.6	13.6 15.7	15.1 20.7	10.2 15.9	15.9 13.8	– 18.5
M.O.R.	N/mm^2	110 °C 1000 °C 1500 °C	19 19 47	10 12 42	10 12 42	9 25 40	11 13 31	19 30 46	9 13 36	14 15 16
C.C.S.	N/mm^2	110 °C 1000 °C 1500 °C	96 101 162	55 57 154	56 79 142	52 155 126	67 87 135	85 143 246	66 100 177	95 131 156
H.M.O.R. at 1500 °C	N/mm^2	1500 °C	1	1	1	0.4	2	3	2	3
R.U.L. T.$_{05}$	°C	1500 °C		1575		1480	1535	1655		1640
P.L.C.	%	1500 °C	−0.4	−0.4	−0.5	−0.8	−1.4	−0.6	−0.7	−0.4

* pre-treatment temperature

shrinkage of the cement free Alphabond bonded castables is somewhat lower due to mullite formation.

The specimens containing 2 % microsilica develop microcracks and slight distortion at 1500 °C.

4.2 Bulk density, apparent porosity

Bulk density and apparent porosity were determined by water immersion method with the dried (unfired) and at 1500 °C/5 h fired samples.

The results (Tab. 5 a – c) show high densification of the vibration and the selfflowing castables with 4.7 – 5.7 % water without addition of microsilica. Also the cement free castables lead to high bulk density at low mixing water content (4.3 – 5.6 %).

On firing at 1500 °C the microsilica free castables develop an apparent porosity of about 17.5 – 21 %, whereas the addition of microsilica up to 2 % decreases porosity down to 15.5 % explanable by the noticable firing shrinkage. The 3 % Alphabond containing castables show similar low apparent porosities than the cement bonded castables with 2 % SiO_2. Otherwise the castable with 6% Alphabond shows an increased apparent porosity of 18.5%.

Between mixing water content and apparent porosity of the microsilica free castables fired at 1500 °C exist a certain correlation (**Fig. 3**). The decrease in water content of about 1% results in a decrease in apparent porosity of about 3%. In SiO_2 containing castables the influence of water content is overlapped by shrinkage processes.

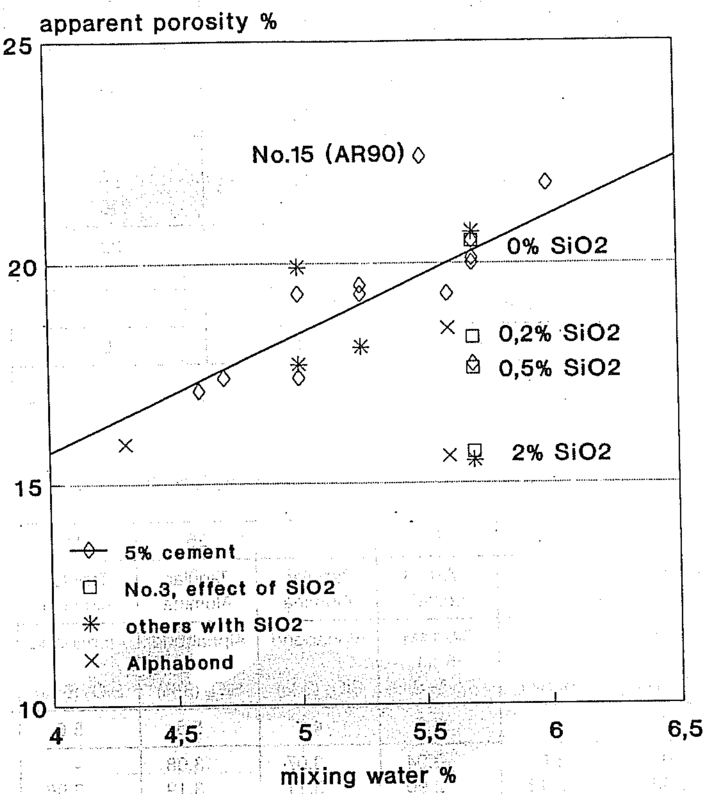

Fig. 3. Relationship between mixing water amount and apparent porosity of tested castables after prefiring at 1500 °C/5 h

4.3 Cold crushing strength (C.C.S.) and cold modulus of rupture (M.O.R.)

The Tab. 5a+b demonstrate the excellent strength properties of the microsilica free vibration and selfflowing castables. Tab. 5c contains the results for castables with addition of microsilica.

The effect of microsilica addition (0.2–2%) on C.C.S. and M.O.R. of cement bonded selfflowing castables can be seen in **Fig. 4.** Similar results were found with the other variations of this castable type and also with the vibration castables.

The strength of cured and dried castables is not influenced by the addition of SiO_2. After firing at 1000 °C a remarkable higher strength is achieved with the addition of 2% microsilica. After firing at 1500 °C the strength is similar high, but there is a trend to lower strength, especially C.C.S., with increasing SiO_2 in the castable despite the lower apparent porosity. This is obvious due to the observed shrinkage and subsequent formation o microcracks.

4.4 Hot modulus of rupture

The hot modulus of rupture was measured on test pieces prefired at 1500 °C/5 h with 1 h soaking time before testing. The results are shown in **Fig. 5.** A typical low cement (5%) bonded Tabular vibration castable (No. 11) has a H.M.O.R. as high as 1 N/mm². A similar composition with a particle size and H_2O content suitable for selfflowing reached only 8 N/mm² (No. 3). Adjusting the water content to vibration consistency in the sam mix increased the H.M.O.R. to 13 N/mm² (No. 1).

Effect of microsilica. The effects of SiO_2 additions to bot types of castables is dramatically. Microsilica in a content as lo as 0.2% dropped the H.M.O.R. to 2 N/mm² (No. 28), respect vely 1 N/mm² (No. 6). Adding 2% microsilica resulted in a even lower strength.

Effect of spinel addition. The addition of AR 78 type spinel i the silica free selfflowing castable did improve the H.M.O.

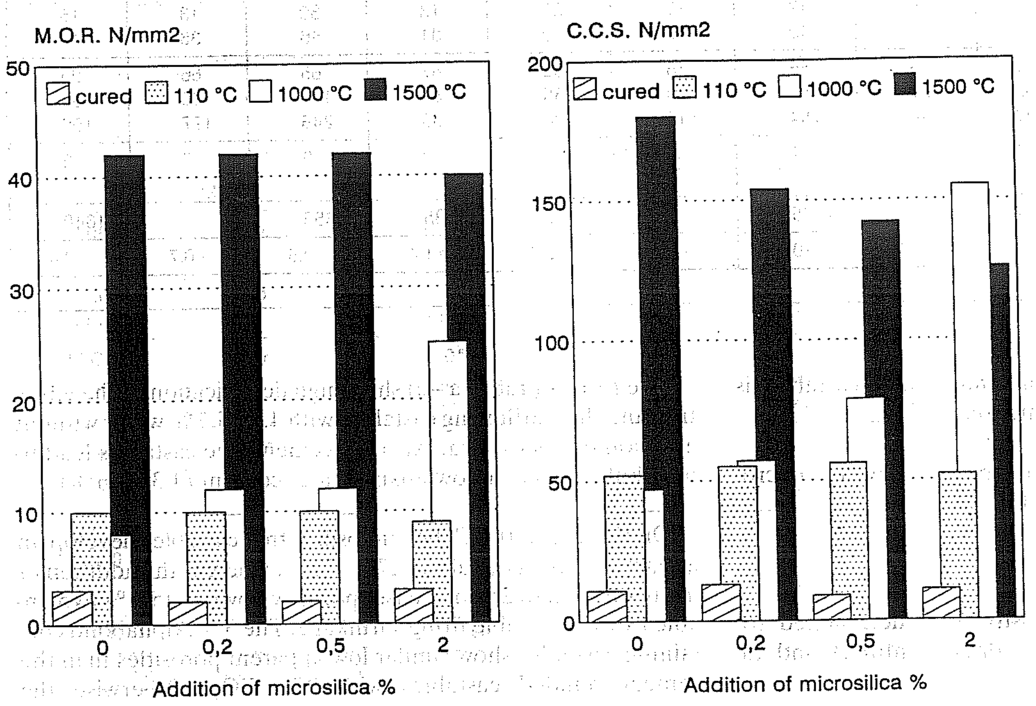

Fig. 4. Effect of microsilica addition on cold modulus of rupt (M.O.R.) and cold crushing streng (C.C.S.) of selfflowing Tabular Alumina castables (5% cement, 5.7% mixing water) after prefirin at 1500 °C/5 h

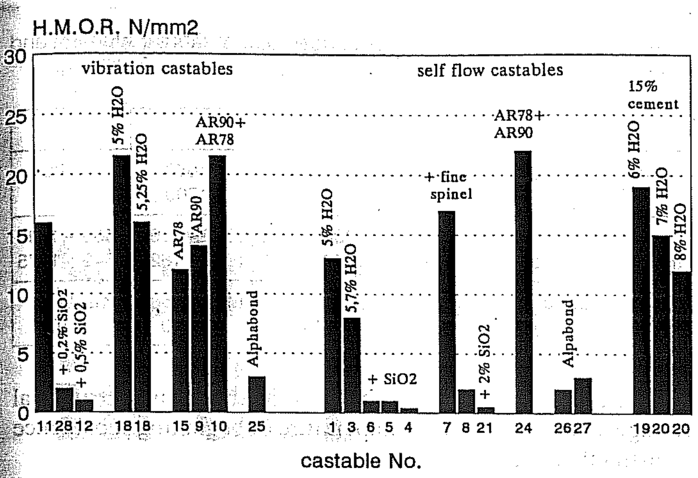

Fig. 5. Hot modulus of rupture (H.M.O.R.) at 1500 °C of selected castables. Test pieces prefired at 1500 °C/5 h, testing at 1500 °C after 1 h holding time

from 8 to 17 N/mm^2 (No. 7). Even further improvement was seen when both types of spinel AR 90 and AR 78 were used. 22 N/mm^2 was the resulting H.M.O.R. (No. 24). Unfortunately the addition of microsilica destroyed this advantage of spinel completely. 0.5 % SiO_2 to No. 7 drops the H.M.O.R. from 17 to 2 N/mm^2 (No. 8). 2 % SiO_2 added lowers the H.M.O.R. from 22 N/mm^2 to 0.5 N/mm^2. The substitution of Tabular Alumina by spinel did not increase the H.M.O.R. Castable No. 9 which contains 85 % AR, 78.5 % cement and 10 % reactive Al_2O_3 had a H.M.O.R. of 14 N/mm^2. Using AR 90 in a similar composition did not change the H.M.O.R. substantially (12 N/mm^2).

Effect of cement type. The newly developed high Al_2O_3 cement in castable No. 18 based on Tabular Alumina gave H.M.O.R. values as high as 21 N/mm^2.

Effect of Alphabond bond. The new bonding system Alphabond based on pure Al_2O_3 in combination with microsilica (castable No. 25–27) results in lower H.M.O.R. values compared to the SiO_2 free cement bonded castables.

Effect of mixing water content. Castables No. 19 and 20 demonstrate once more clearly the influence of casting H_2O on the H.M.O.R. of selfflowing conventional cement castable. The 19 N/mm^2 which were measured at 6 % H_2O (vibration consistency) drops to 15 N/mm^2 when casted under selfflowing conditions with 7 % H_2O. By adding 1 % more water a further decrease to 12/mm^2 can be seen.

Fig. 6 shows the results on the H.M.O.R. as a function of temperature of castable No. 11, 12 and 25. Castable No. 11, a pure cement bonded system increases its H.M.O.R. between 1000 °C and 1400 °C, followed by a slight decrease to 1500 °C. Adding 0.5 % microsilica to this castable yield slightly higher strength at 1100 °C. However at 1200 °C the SiO_2 free castable shows already a better performance. A dramatic decrease of strength of the SiO_2 containing castable can be seen above 1300 °C.

Surprisingly high was the H.M.O.R. of the 3 % Alphabond + 3 % SiO_2 containing castable No. 25 at 1100 °C. With 30 N/mm^2 it was twice as high as the similarcement bonded species. At 1200 °C the cement bonded system outperformed also castable 25. Remarkable is that at 1500 °C when the SiO_2 containing cement bonded castable is showing a clear trend to reach values close to 0, the Alphabond containing castable retains a higher strength.

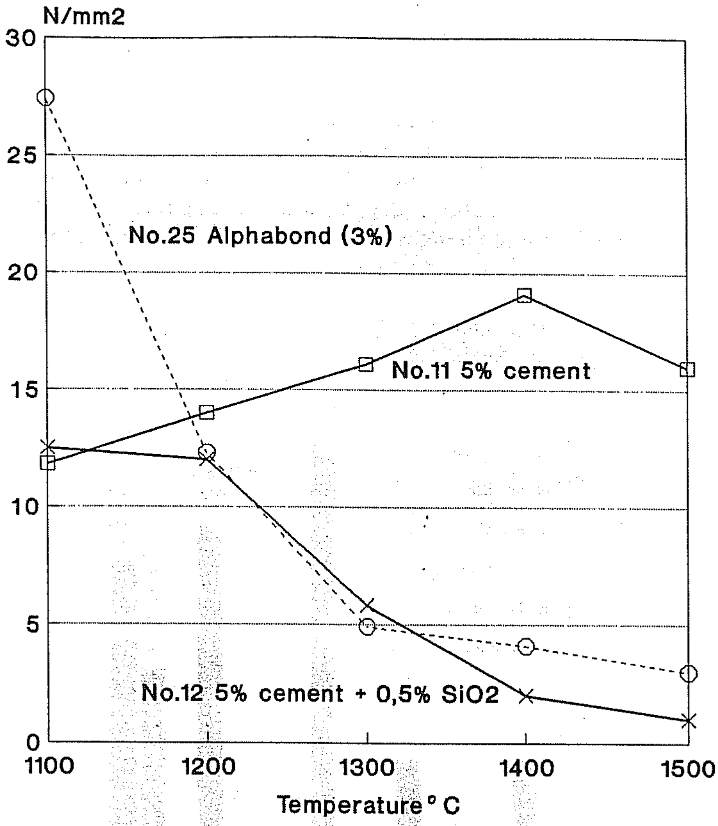

Fig. 6. Temperature dependence of hot modulus of rupture of a pure cement bonded Tabular Alumina castable without and with an addition of 0.5 % microsilica and bonded with the Alphabond system. Prefiring of test pieces 5 h on testing temperature

Unfortunately H.M.O.R. at temperatures above 1500 °C could not be measured.

4.5 Hot crushing strength

To gain more information on the performance at higher temperatures than 1500 °C and to compare castables with bricks, the hot crushing strength (H.C.S.) at 1650 °C of selected materials has been measured by M. Koltermann and M. Buhr [7]. The target of the investigation of M. Koltermann et al. was to identify refractory materials suitable for steel ladles or other high temperature applications with service temperatures ≥ 1650 °C. **Fig. 7** shows the results of bricks and castables. The tests have been performed with the same equipment. All tested SiO_2 free cement bonded castables outperformed all bricks by far. The pure corundum brick has at 1650 °C a H.C.S. of 4–5 N/mm^2. This compares to the cement bonded system which had a H.C.S. of 43 N/mm^2. Dramatically again the effect of 0.5 % SiO_2. It drops the H.C.S. to 2 N/mm^2. Spinel addition does not improve hot crushing strength. Substitution of Tabular Alumina by pure spinel even reduces it. Selfflowing castables behave similar but have a lower hot crushing strength due to the higher mixing water content.

4.6 Refractoriness under load (R.U.L.)

Refractoriness under load was determined according DIN 51053 Part 1. Unfired (dried) and at 1500 °C prefired test cylinders were tested with a load of 0.2 N/mm^2. The testing of unfired material gives an indication of changes in the material on first heating up. Testing after prefiring describes the softening behaviour of the "ceramically stabilized" material.

The range of R.U.L. values of the tested castable types are summarized in **Tab. 6. Fig. 8a–g** illustrate the thermal expansion/subsidence behaviour of selected castables.

The first heating up of the SiO_2 free castables results in a wavy curve beginning at about 1250 °C, which can be refered to a beginning of texture changes by formation of CA_6. The "stabilized" texture of the prefired shows no further sign of structural changes. As expected the temperature of beginning subsidence is distinctly higher.

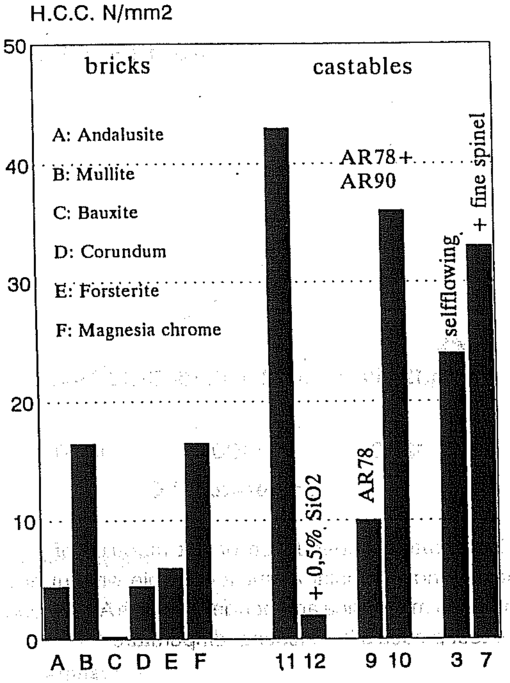

Fig. 7. Hot crushing strength (H.C.C.) of bricks and castables at 1650 °C

Tab. 6. Ranges of refractoriness under load of Tabular Alumina and spinel castables

bond		T_{05} °C	T_1 °C	T_2 °C
cement (5 %)	unfired	>1615	<1680	>1700
	fired 1500 °C	>1650	>1700	
cement (5 %) + microsilica (0.2–2 %)	unfired	1330 – 1390	1370 – 1390	1430 – 1590
	fired	1480 – 1575	1510 – 1620	1540 – 1675
Alphabond (3–6 % SiO_2)	unfired	ca. 1370	1470 – 1580	ca. 1690
	fired	~ 1490	~ 1650	~ 1700

Effect of microsilica. Already the small addition of 0.2% microsilica remarkably reduces the temperature of beginning subsidence and the R.U.L. values on the first heating up. The wavy character of the curves seen with the SiO_2-free castables is not present. After prefiring at 1500 °C/5 h the R.U.L. values are distinctly lower than that of the SiO_2 free castables, as demonstrated in **Tab. 7.**

Effect of spinel addition. The character of the R.U.L. curve of the unfired material is not changed significantly by the addition of fine spinel AR 78. The comparison of microsilica free prefired castables without and with spinel addition seems to confirm that fine spinel stabilizes the matrix phase resulting in a higher temperature of beginning softening (see Fig. 8c).

The complete substitution of tabular alumina by AR 90 spinel (Fig. 8d) doesn't change noticably the softening behaviour of the castable on the first heating up, but prefiring results in a very high refractoriness under load. A small after-expansion is evident before beginning of subsidence.

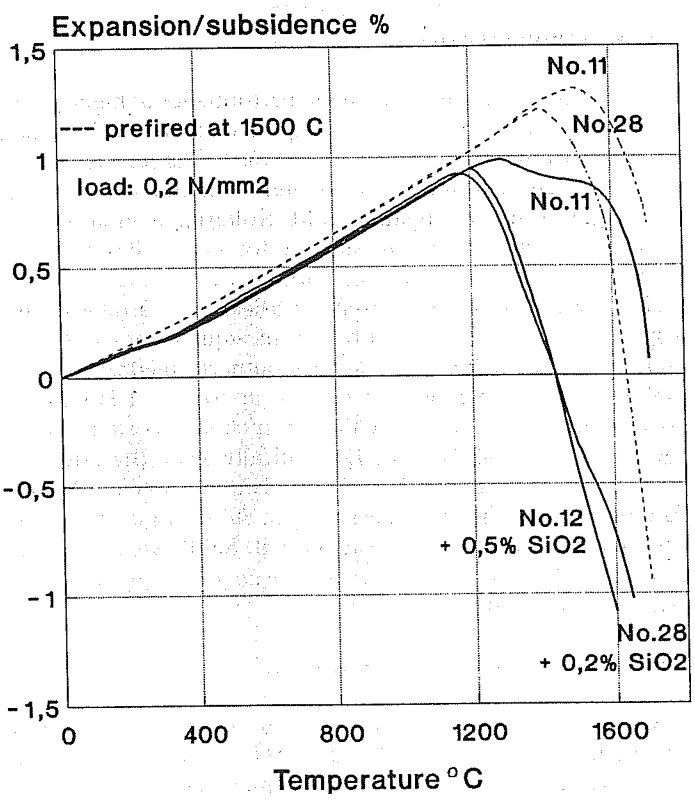

Fig. 8a. R.U.L. curves of vibration Tabular Alumina castables

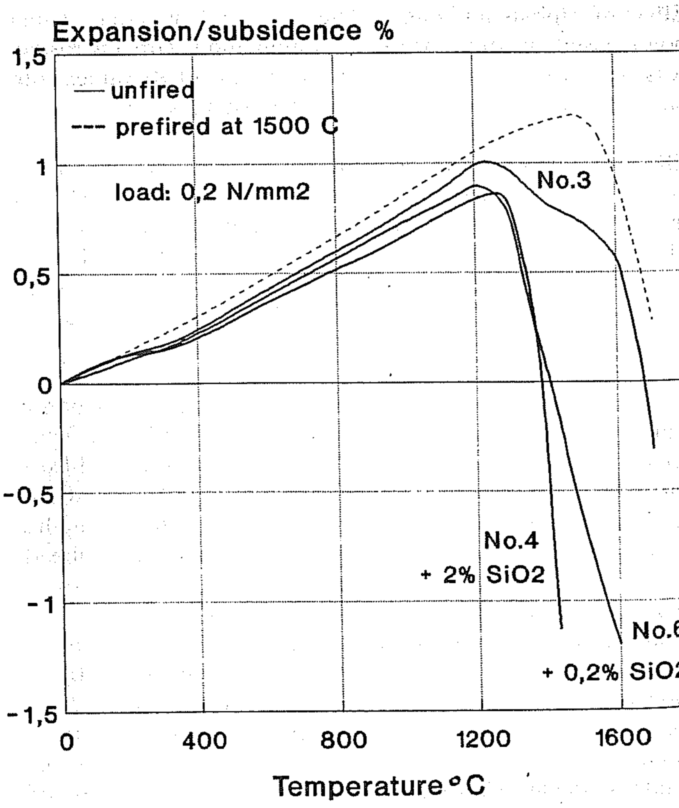

Fig. 8b. R.U.L. curves of selfflowing Tabular Alumina castables

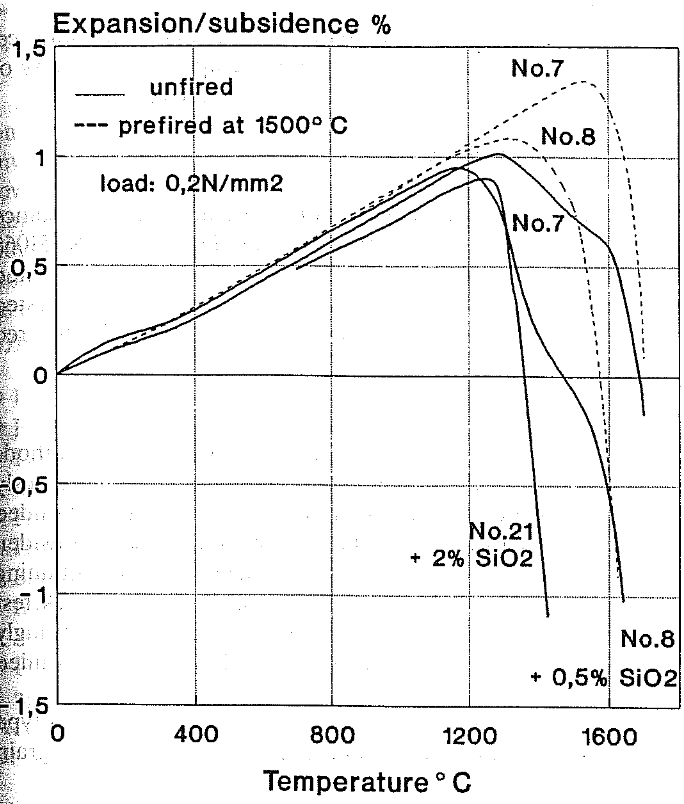

Fig. 8c. R.U.L. curves of selfflowing Tabular Alumina castables with addition of 20 % fine spinel (AR78)

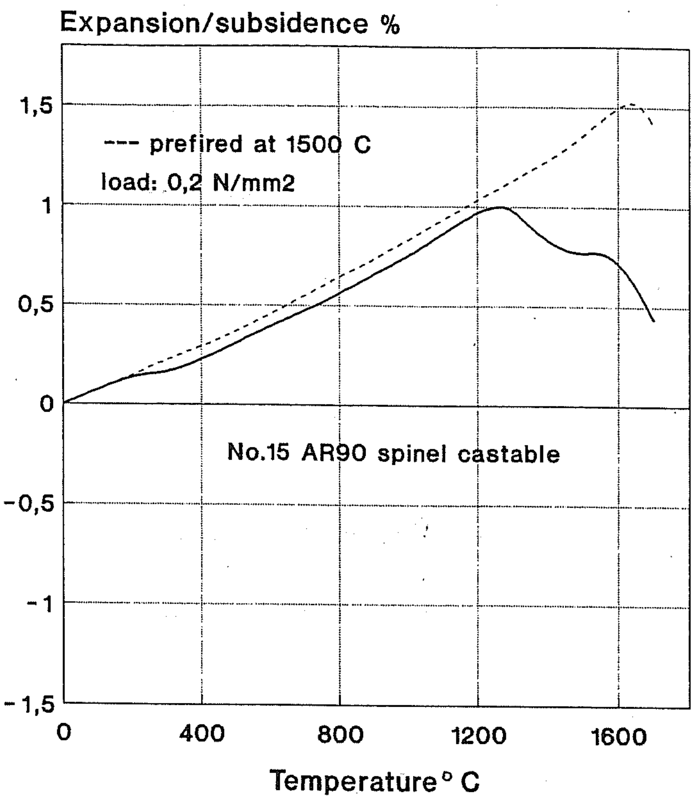

Fig. 8d. R.U.L. curve of the vibration AR90 spinel castable No. 15

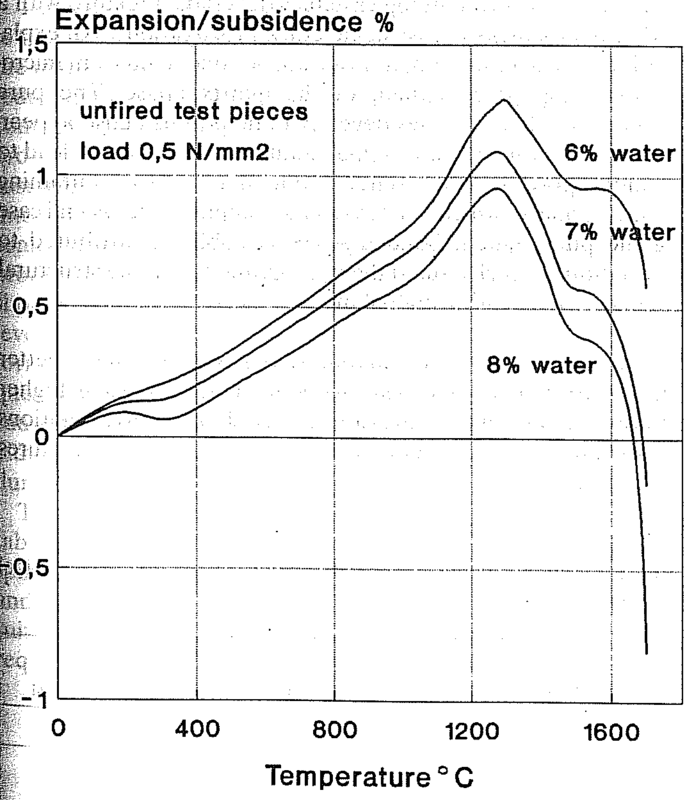

Fig. 8e. Influence of mixing water amount on the R.U.L. curve of a 15 % cement Tabular Alumina castable

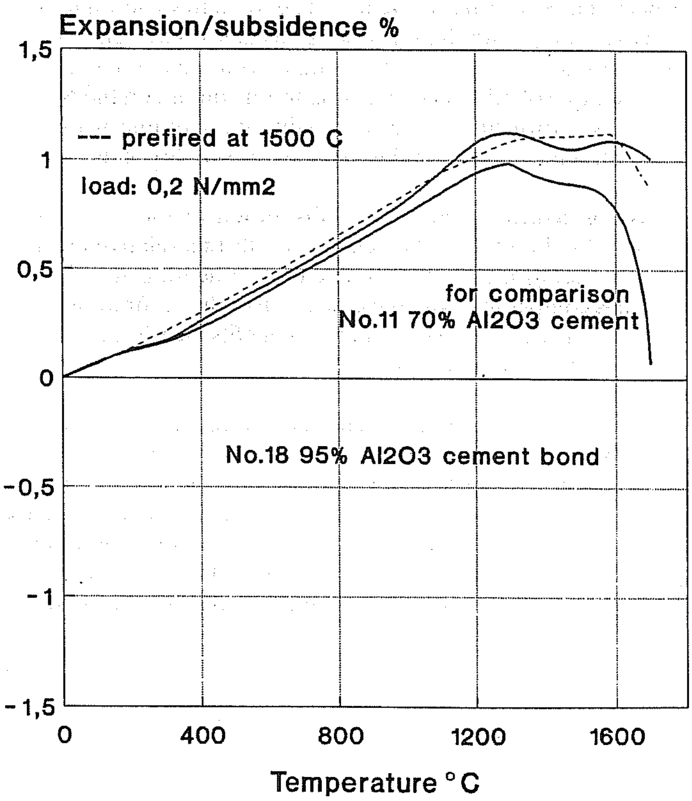

Fig. 8f. R.U.L. curve of the vibration 95 % Al_2O_3 cement bonded Tabular Alumina castable No. 18

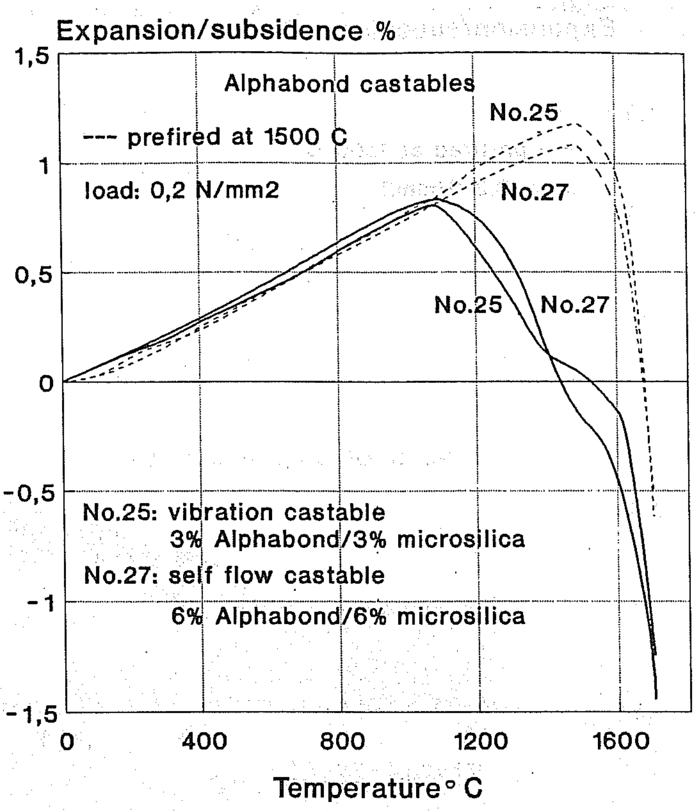

Fig. 8g. R.U.L. curves of Alphabond system bonded castables

Effect of mixing water content. The trend to some what lower R.U.L. values with the selfflowing castables is evident and can be attributed to the about 0,7 % higher content of mixing water. An example of influence of mixing water content on the R.U.L. curve is shown in Fig. 8e for a vibration castable with 15 % cement. A high water content weakens the stability of the matrix.

Effect of cement type. The substitution of the 70 % Al_2O_3 cement by the 95 % Al_2O_3 cement results in a relative even expansion behaviour of the castable on first heating up (Fig. 8f), which is comparable with the expansion of the prefired castable. The use of the 95 % Al_2O_3 cement benefits clearly the volume stability at high temperatures.

Effect of Alphabond bond. The cement free castables with the addition of 3 % resp. 6 % Alphabond and 3 % resp. 6 % microsilica show a more or less steady subsidence on first heating up (Fig. 8g). The lower subsidence rate in the temperature range around 1400 °C can be attributed to the formation of mullite. A comparison of the characteristic R.U.L. values shown in **Tab. 6** clearly demonstrate the higher temperature stability of Alphabond bonded castables compared to the SiO_2 containing cement bonded castables. Still the high temperature stability of SiO_2 free cement bonded castables is not reached.

Tab. 7. Influence of microsilica addition on refractoriness under load of the base selfflowing castable

Castable No.	unfired °C			prefired at 1500 °C / 5 h °C		
	T_{05}	T_1	T_2	T_{05}	T_1	T_2
3	1615	1680	>1700	1660	>1770	
6 (+ 2 % SiO_2)	1340	1425	1585	1575	1620	1675
4 (+ 2 % SiO_2)	1365	1390	1430	1480	1510	1540

4.7 Thermal shock resistance

A practice orientated evaluation of thermal shock resistance is difficult. Nevertheless the two standardized DIN 51068 methods – water quenching and air quenching of 950 °C heated test pieces – were used to get a rough rating of the tested castables. The tests were conducted with at 1500 °C/5 h prefired specimens.

The summarized results are in **Tab. 8.**

The best thermal shock performance for both test methods were found with the Alphabond bonded castables. Obviously the formation of mullite as known from the mullite bonded corundum bricks enhances thermal shock resistance considerably. Despite the poor hot performance of SiO_2 containing cement bonded castables their behavior in thermal shock test results was comparable to the Alphabond system. Surprisingly good performance was reached by AR90 cement bonded castable.

Vibration castables have better values than selfflowing type explanable by the lower water content and lower fine grain content.

The crack formation and rupture of the castables without and with microsilica addition is very different. The microsilica free castables normally form more or less straight cracks, which leads to the breaking of the test pieces (catastrophical rupture). The microsilica containing castables develope a texture with a lot of microcracks (quasi stable crack propagation). An explanation of this different behaviour can be conducted from microtexture resp. development of the matrix phase. The pure cement bonded castables develop a fine porous dense appearing matrix, while already a small addition of microsilica lead to a more porous, more sintered and micro-crack containing bonding phase, which reacts as a crack stopper. The special case of the pure cement bonded AR90 castables is attributed to formation of cracks round the large grains due to the structural change when heating high-alumina spinels.

The advantage of the alumina-spinel system to have better hot performance might lead to better behavior when higher thermal shock temperatures are applied. Further investigations on the influence of higher prefiring and quenching temperatures are required.

Tab. 8. Thermal shock resistance of Tabular Alumina and spin castables

castable type	cycles	
	water quenching	air quenching
cement (15 %) selfflowing	2	2
cement (5 %) vibration	3 – 6	>9
cement (5 %) selfflowing	2 – 6	3 – 7
cement (5 %) AR90 spinel	>7	>10*
cement (5 %) + microsilica (0.2 – 2 %)	>8	>10*
Alphabond (3 – 6 % SiO_2)	>10*	>10*

* not further tested

5. Discussions and Conclusions

For the optimum design of high performance castables based on high purity synthetic alumina aggregates, the results of this investigation on properties at high temperature of high alumina low cement castables can be used for orientation. Referring to slag attack it was proved [8] that the use of alumina rich spinels improve slag resistance remarkably. Depending on the application requirements different castable designs should be targeted as follows:

Type of application requirements	Recommended Castables
• High hot strength without slag attack	A, E
• High hot strength with slag attack	B, C
• High thermal shock resistance and high hot strength	C
• High thermal shock resistance, medium H.M.O.R. and slag attack	D
• Slag attack, high hot strength and high thermal shock resistance	C
• Application temperature > 1700 °C	E (A)
• High thermal shock resistance and application-temperature < 1300 °C.	F

A: Low cement bonded Tabular Alumina castable
B: Low cement bonded Tabular Alumina Spinel (AR 78/AR 90) castable
C: Low cement bonded spinel (AR 90) castable
D: Alphabond/microsilica Tabular Alumina Castable
E: High Aluminum Cement bonded Tabular Alumina castable
F: LC-castable with microsilica

The results of H.M.O.R., H.C.S. and R.U.L. clearly indicate that for applications above 1300 °C the use of microsilica in the matrix of L.C.C. is not of advantage because of drastically reduced hot properties. It is clear that by reducing the cement content down to a CaO level ≤ 0.5 % this results could be improved [1]. But it is questionable if the use of ultra low cement castables is recommendable with high purity aggregates, taking into an account the demonstrated performance data of low cement castables without silica. Also the problems of setting reproducibility, green strength and flow consistency of U.L.C.C.s should be considered. The described results indicate that silica levels as low as 0.2 % have a detrimental effect on the hot performance of LC-Tabular Alumina castables. This brings up the question how often unexpected failures of refractories in use is caused by silica impurities. These impurities can be introduced either by unsuitable raw materials or by cross contamination during production.

The exceptional hot performance of pure cement bonded tabular castables can even be more improved by the addition of spinel. A combination of a spinel type containing 90 % alumina and a spinel type containing 76–77 % alumina seems to be most suitable. When hot performance together with slag resistance is required the addition of spinel seems to be the best alternative.

Since the results also indicate that there is a strong correlation between mixing water content and hot performance it has to be emphazised that precision in controlling water amount, but also grain size distribution and also appropriate processing (sufficient mixing homogenity) is required for optimum results.

In applications where only medium hot strength but high slag resistance is needed, the pure alumina Alphabond binder together with microsilica can be a good alternative.

If thermal shock resistance and good hot performance together with high slag resistance is needed, the use of tabular-alumina free cement bonded AR 90 spinel castables give clearly the best results.

The new developed high alumina cement with an alumina content of 95 % is the material of the choice when very high application temperatures are required.

For applications where the temperature does not exceed 1300 °C and high thermal shock resistance is required it seems that microsilica addition to low cement tabular alumina castables can be of use. However it is a question, if this is the commercially most suitable approach.

Comparing the results of the hot crushing strength of castables versus bricks, it has been demonstrated that castables can outperform bricks clearly at temperatures as high as 1650 °C. It should also be noted that selfflowing castables have proved their usefulness also in high temperature applications. (FF 35)

References

[1] *Myhre, B.:* Hot strength and bond-phase reactions in low and ultra-low-cement castables. In: Proceedings UNITECR '93 Congress, São Paulo 1993, p. 583–594

[2] *Myrhe, B.:* Strength development of bauxite – based ultra low cement castable. Am. Ceram. Soc. Bull. 73 (1994), 5, 68–73

[3] *Krönert, W.; Schumacher, U.:* New developments on low- and ultra-low cement castables. Spec. Issue Interceram, Aachen Proceedings 1988, p. 12–18

[4] *MacZura, G. et al.:* Development technical refractory materials – Part I. Presented at the 2nd. Intern. Conference on Refractories, Tokyo, Japan (1987)

[5] *MacZura, G. et al.:* Development technical refractory materials – Part III. UNITECR '91 Congress, Second Edition. Verlag Stahleisen, Düsseldorf (1992), p. 392–396

[6] *Eto, S. u. a.:* Effect of CaO content on the properties of alumina-spinel castable for steel ladle. In: Proceedings UNITECR '93 Congress, Sao Paulo 1993, p. 1289–1300

[7] *Koltermann, M.; Buhr, A.; Siggelkow, K.:* Erhöhung der Haltbarkeit von Stahlgießpfannen durch Einsatz von neuem und verbessertem Feuerfestmaterial. Abschlußbericht 72010-CE/102 (C5.1/88) der Europäischen Gemeinschaft für Kohle und Stahl (1992)

[8] *Kriechbaum, W. G.; Wöhrmeyer, Ch.; Routschka, G.:* Neue Spinell-Rohstoffe für Feuerfestauskleidungen im Stahlbereich. Vortrag auf dem XXXV. Internationalen Feuerfestkolloquium Aachen, 1992 (Sonderdruck der Fa. Alcoa Industrial Chemicals Europe, Bad Homburg)