Reprint from STAHL UND EISEN Special 1996 – XXXIXth International Colloquium on Refractories, pages 211–218

The Matrix Advantage System, a new approach to low moisture LC selfleveling alumina and alumina spinel castables.

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Abstract

New fine Aluminas, fine Spinels and a Calcium Aluminate cement have been developed as part of the **'Matrix Advantage System'** (MAS). The MAS has allowed the development of low moisture selfleveling castables with controlled but flexible placement properties in a wide temperature range. The water demand to achieving selfleveling flow performance of such castables, with a 5% cement addition, is 4,0 – 4,7%. The major physical and mechanical properties of these castables and the corrosion behavior of selected castables against basic slag has been tested. The placement, setting and flow properties in a temperature range between 7 – 35 °C are demonstrated.

1. Introduction

Due to the superior placement properties, when compared with vibration castables, the consumption of selfleveling castables has increased considerably. Applications such as monolithic ladle linings – where pumpability of the refractory material is critical for quick and easy installment – have strongly influenced the use of selfleveling monolithic systems. For the production of selfleveling castables the refractory industry has so far had to use raw materials which have not been specifically designed and optimized for the needs of selfflowing systems. This raises the question if the mechanical properties and application performance of selfleveling castables can be further improved when raw materials that are optimised for these systems are used.

Key problems the refractory producer and installer face when a cement bonded selfflowing castable is fabricated and applied are:

- Strong influence of temperature on flow time, setting time and demolding time
- Differences in plant sites and applications, requiring quite different but controlled placement and demolding times
- Dilatant flow behavior of selfflowing castables complicates handling and dosing
- Water demand of selfleveling systems is still considerably higher than for vibration castables
- Strong decrease of mechanical strength and corrosion resistance if over-watering occures
- Variations in cement reactivity influence placement and setting time strongly

This paper describes a group of newly developed fine materials, the **"Matrix Advantage System"** which consists of Reactive Alumina, Reactive Alumina/Spinel, Calcium Aluminate Cement and Dispersing Aluminas. All these materials have been specifically optimised in particle size distribution, morphology and chemistry for the needs of low moisture selfleveling cement bonded Alumina and Alumina-spinel castables. These materials have been used in model castables with 5% cement. The temperature influence on placement and setting properties has been investigated. The major mechanical and physical properties, and corrosion behavior, of these castables against basic slag are demonstrated. On selected formulations H.M.O.R. at 1500 °C and Refractoriness under Load have been analysed.

2. Raw Materials and Castables

The established raw materials used are Tabular Alumina T-60 and AR78 and AR90 Alumina-rich Spinels **(Tab. 1)**. The properties of the new developed raw materials and their specific functions are shown in **Tab. 2.**

The Reactive Alumina CTC 50 and Alumina-Spinel CTC 55 have a quadromodal particle size distribution to achieve a continuous curve of particle size distribution in the range below 45µm **(Fig. 1a + b)** and therefore excellent flowability and high packing density of the castable.

Tab. 1. Chemical composition of used established raw materials

	Tabular Alumina T-60	Spinel AR 90	Spinel AR 78	Reactive Alumina CL 370 C	70% Alumina Cement CA-14 M
Al_2O_3 [%]	99,4	89 – 90	76 – 77	99,8	72,7
Na_2O [%]	0,36	< 0,17	< 0.15	0,06	0,19
CaO [%]	0,05	< 0,25	< 0,3	0,02	26,5
MgO [%]	< 0,10	9 – 10	22 – 23	0,02	0,09
SiO_2 [%]	0,02	< 0,05	< 0,06	0,03	0,2
Fe_2O_3 [%]	< 0,10	< 0,10	< 0,10	0,03	0,11

Tab. 2. Properties of the components of the new developed **Matrix Advantage System**

Type	CTC 50 Reactive Alumina	CTC 55 Reactive Alumina Spinel	ADS 1 Dispersing Alumina	ADW1 Dispersing Alumina	CA-270 Calcium Aluminate Cement
Al_2O_3 [%]	99,5	90,5	80,0	80,0	72 - 74
Na_2O [%]	0,15	0,12	0,15	0,15	0,16
CaO [%]	0,03	0,10	2,0	2,0	25 - 27
MgO [%]	0,04	8,0-9,0	n.d.	n.d.	0,09
SiO_2 [%]	0,06	0,08	n.d.	n.d.	0,14
Fe_2O_3 [%]	0,03	0,04	n.d.	n.d.	0,10
B_2O_3 [%]	-	-	0,8-1,0	0,03	n.d.
L.O.I. [%] (1050 °C)	-	-	17,0	17,0	n.d.
BET [m^2/g] spec.surface	4,0	4,0	n.d.	n.d	1,5
D50-Cilas [µm]	1,5	1,5	2,4	2,4	6
D90-Cilas [µm]	8,5	8,5	6,6	6,8	48
Key functions	- high matrix refractoriness		- dispersing and reduction of water demand		- hydraulic bonding
	- ceramic bonding		- retard setting setting	- accelerate bonding	- ceramic bonding
	- optimize particle packing		- control placement and setting at low, ambient and high temperatures		- CA_6 formation
		-corrosion resistance	- ceramic bonding		

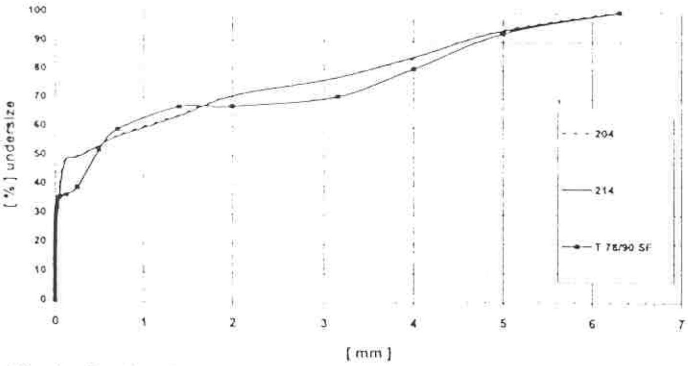

Fig. 1a. Particle Size Distribution of castables 204 and 214 in comparison to the conventional selfflowing castable T78/90 SF

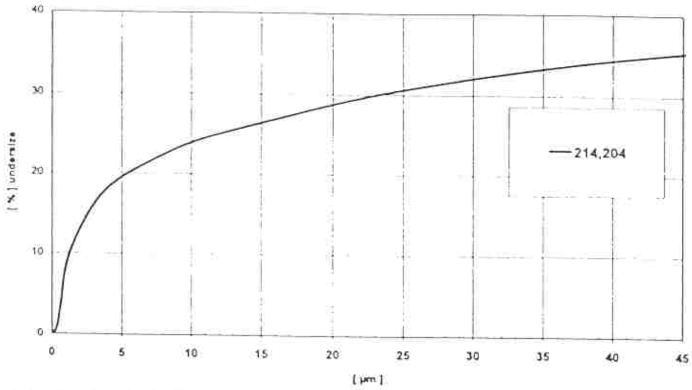

Fig. 1b. Particle Size Distribution of the -45µm portion of castable 214, 204

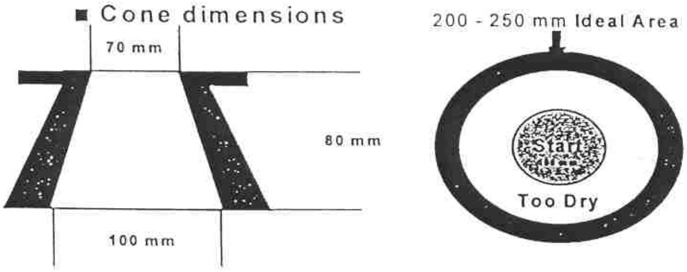

Fig. 2. The selfflow cone test

The two dispersing Aluminas, ADS 1 and ADW 1, have bimodal size distributions and contain organic ingredients to improve dispersion and allow setting characteristics to be controlled. ADS 1 has been specifically designed to improve dispersion and give controlled retarding properties in a cement bonded system, ADW 1 also improves dispersion but offers the option to accelerate the setting of a cement bonded castable.

Tab. 3a and 3b show the compositions of the tested LC Tabular Alumina and Tabular Alumina-Spinel selfleveling castables, with 5% cement, using the new **Matrix Advantage System.** For comparison a vibration castable (Vib. 215) using the **Matrix Advantage System**, and a conventional selfflowing castable (T78/90SF) were also tested.

3. Preparation of test pieces and testing

All ingredients are mixed dry for 1 minute. After water addition mixing is continued for a further 4 minutes. The castable is then cast into molds without compacting or vibration. The cast test pieces are immediately cured at 32 °C/24h in a climate cabinet (min. 90% relative humidity). Samples which are tested at specific temperatures are also cured at these temperatures. **Tab. 4** gives an overview of specimen size, pre-treatment and test methods.

Tab. 3a. Composition of new developed selfleveling LC Tabular Alumina and Tabular Alumina-Spinel (15 – 17%) castables

Type	Tabular Alumina castable	Tabular Alumina - Spinel Castables	
Castable / Component	204	214	210*
Tabular Alumina T-60 [%]	78	69	59
Spinel AR 78 [%]	-	9	19
Reactive Alumina CTC 50 [%] Alumina/Spinel CTC 55 [%]	17 -	- 17	- 17
Cement CA-270 [%]	5	5	5
Total [%]	100	100	100
Dispersing Al_2O_3 [%] ADS 1	0,5 1,5	0,5 1,5	1,5
ADW 1	0,5 -	0,5 -	-
Mixing water [%]	4,0 4,7	4,2 4,7	4,7

Tab. 3b. Composition of new developed selfleveling LC Tabular Alumina Spinel castables with > 20% Spinel

Type	Tabular Alumina-Spinel (> 20% Spinel)				
Mix	224	225	226	T78/90SF*	Vib. 215
Tabular Alumina [%]	52	58	58	60	59
Spinel AR 78 [%]	26	9	20	15	19
Spinel AR 90 [%]	-	11	-	10	-
Reactive Alumina CL 370 C [%]	-	-	-	10	-
Reactive Alumina/ Spinel CTC 55 [%]	17	17	17	-	17
Cement [%] CA-270 CA-14 M	 5 -	 5 -	 5 -	 - 5	 5 -
Total [%]	100	100	100	100	100
Dispersing Al_2O_3 [%] ADS1 ADW1	 0,5 0,5	 0,5 0,5	 0,5 0,5	 - -	 1,0 -
Darvan [%] Citric acid [%]	- -	- -	- -	0,15 0,07	- -
Mixing water [%]	4,2	4,2	4,2	5,8	3,7

* conventional selfflowing castable ** vibration castable

To determine the mixing water content of the selfleveling castables and to determine their flowability, the **selfflow-cone test** was used **(Fig. 2):**

Immediately after wet mixing (4 min) the castable is cast in batches of about 1,5kg each into metal flow cones (dimensions see Fig. 2). The self-flow cones are completely filled.

For the self-flow test a cone is lifted up after 10 min, 30 min and 60 min and so on after water addition, until no flow is reached. The castable is termed self-flowing when it exhibits the ability to spread out evenly on its own without the application of any external forces. The mix should flow homogeneously and without segregation of water or fines at the outer rim. For the 10min. tests a median flow diameter of 200 – 250mm should be reached (Fig. 2). After 30min the flow diameter should be at least 190mm. During the tests it is important to maintain a constant ambient and castable temperature, i.e. 20 °C. The actual temperature is noted with the flow test results.

4. Physical properties

Properties of the tested castables are compiled in **Tab. 5a – b.**

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

Specimen size	Pre-treatment	Measured properties	Test method
40x40x160mm	cured at 32°C/24h 110 C/24h 800 °C/5h 1000 °C/5h 1500 °C/5h 1650 °C/5h	permanent linear change (PLC) cold modulus of rupture (MOR.) cold crushing strength (CCS) bulk density, apparent porosity pore size distribution	DIN 51010 resp. 26.-28. PRE-Recommendation (EN 1402)
25 x 25 x 150 mm	1500 °C/5h	hot modulus of rupture (H.M.O.R.)	DIN 51048, part 1 restp. 18. PRE-Recommendation
54 x 64 x 230 mm	110 °C/24h 1500 °C/5h 1650 °C/5h	refractoriness under load (RUL) thermal shock resistance (air quenching)	DIN 51053, part 1 resp. ISO 1893 DIN 51068, part 2 resp. 5. PRE-Recommendation
h = 270 mm d = 25 mm 8 segments in one crucible outer diameter = 175 mm inner diameter = 150 mm	1000 °C/5h	Corrosion resistance 1650 °C/6h	Induction furnace test, 10000 Hz Steel: ST37, 15 kg Slag: C/S=2,0 3x1,0kg

Tab. 5a. Properties of new developed selfleveling LC Tabular Alumina and Tabular Alumina-Spinel (15 – 17%) castables

Type	Pre-treatment	Tabular Alumina castable		Tabular Alumina-Spinel (15-17%) castable		
Castable		204		214		210**
Mixing water [%]		4,0	4,7	4,2	4,7	4,7
Bulk density (by weighing and measuring) [g/cm³]	*110 °C	3,20	3,19	3,16	3,11	3,06
	800 °C	3,17	3,16	3,09	3,06	3,07
	1 000 °C	3,15	3,14	3,08	3,08	3,00
	1500 °C	3,12	3,13	3,07	3,09	3,09
	1650 °C	3,18	3,20	3,15	3,10	3,14
Bulk density (by water absorption) [g/cm³]	110 °C	3,23	3,23	3,18	3,15	3,09
	1 500 °C	3,17	3,17	3,13	3,11	3,11
	1650 °C	3,24	3,22	3,17	3,15	3,11
Apparent porosity [vol.%]	110 °C	11,6	11,9	10,0	12,9	14,3
	1 500 °C	15,9	16,1	16,3	17,4	17,3
	1650 °C	14,0	14,7	14,6	15,3	16,4
Modulus of rupture (M.O.R.) [N/mm²]	cured 32 °C	4,5	4,0	4,9	3,4	1,2
	110 °C	17,2	14,5	14,3	8,4	7,5
	800 °C	8,0	11,1	11,3	6,9	5,3
	1 000 °C	13,9	8,8	11,8	6,9	5,5
	1500 °C	56,1	52,1	65,6	44,6	33,5
	1 650 °C	55,0	60,9	69,0	56,2	46,6
Hot modulus of rupture (H.M.O.R.) at 1500 °C [N/mm²]	1500 °C	19,9	17,1	23,0	25,0	13,1
Cold crushing strength (C.C.S.) [N/mm²]	cured 32 °C	26,7	25,0	35,3	20,0	16,1
	11 0 °C	100,9	108,0	104,0	77,0	63,5
	800 °C	79,9	123,5	135,0	94,0	75,5
	1 000 °C	94,3	68,5	88,0	62,5	50,5
	1 500 °C	343,4	254,9	329,1	235,6	210,1
	1650 °C	359,5	282,5	349,7	275,3	229,8
Permanent linear change (P.L.C.) [%]	11 0 °C	± 0	± 0	- 0,1	± 0	± 0
	800 °C	- 0,05	± 0	± 0	- 0,06	- 0,07
	1000 °C	+ 0,01	+ 0,02	- 0,1	- 0,08	- 0,08
	1500 °C	+ 0,1	- 0,03	- 0,1	- 0,10	- 0,22
	1650 °C	- 0,6	- 0,44	- 0,5	- 0,37	- 0,43

* pre-treatment ** addition of 0,2% $Al(OH)_3$ + 0,2% Al powder

Tab. 5b. Properties of new developed selfleveling LC Tabular Alumina-Spinel castables (> 20% Spinel)

Type	Pre-treatment	Tabular Alumina-Spinel castable (> 20% Spinel)				
Castable		224	225	226	Vib. 215[1]	T78/90SF
Mixing water [%]		4,2	4,2	4,2	3,7	5,8
Bulk density (by weighing and measuring) [g/cm³]	110 °C	3,10	3,08	3,04	3,10	3,07
	800 °C	3,02	3,06	3,01	3,11	2,94
	1000 °C	3,06	3,06	3,06	3,08	3,05
	1500 °C	3,00	3,08	3,04	3,09	3,03
	1650 °C	3,06	3,05	3,07	3,09	2,99
Bulk density (by water absorption) [g/cm³]	110 °C	3,07	3,09	3,06	3,12	3,03
	1500 °C	3,04	3,05	3,03	3,11	2,98
	1650 °C	3,08	3,08	3,08	3,14	2,99
Apparent porosity [vol.%]	110 °C	14,7	14,0	14,5	12,5	15,8
	1500 °C	17,6	18,3	18,3	15,7	20,0
	1650 °C	15,7	16,6	16,2	14,3	18,8
Modulus of rupture (M.O.R.) [N/mm²]	cured 32 °C	3,3	3,3	4,2	4,8	1
	110 °C	10,3	10,7	10,3	15,8	5
	800 °C	4,2	8,0	8,8	9,1	4
	1000 °C	8,2	7,0	7,5	10,1	6
	1500 °C	48,5	49,5	49,3	62,0	24
	1650 °C	48,4	55,6	53,5	57,0	26,5
Hot modulus of rupture (H.M.O.R.) at 1500 °C [N/mm²]	1500 °C	24,5	22,2	25,3	32,7	15,0
Cold crushing strength (C.C.S.) [N/mm2]	cured 32 °C	22,5	20,4	22,0	35,0	6,0
	110 °C	72,5	68,5	66,0	95,3	35,0
	800 °C	50,0	68,5	70,5	121,5	37,8
	1000 °C	64,0	61,0	61,0	110,0	40,2
	1500 °C	263,0	265,0	257,0	333,8	130,0
	1650 °C	297,0	279,0	294,0	331,9	116,5
Permanent linear change (P.L.C.) [%]	110 °C	± 0	- 0,06	± 0	± 0	- 0,06
	800 °C	- 0,09	- 0,09	- 0,06	- 0,1	- 0,07
	1000 °C	- 0,03	- 0,06	± 0	± 0	± 0
	1500 °C	- 0,09	- 0,06	± 0	± 0	- 0,06
	1650 °C	- 0,53	- 0,5	- 0,53	- 0,3	- 0,53

[1] Vibration Castable

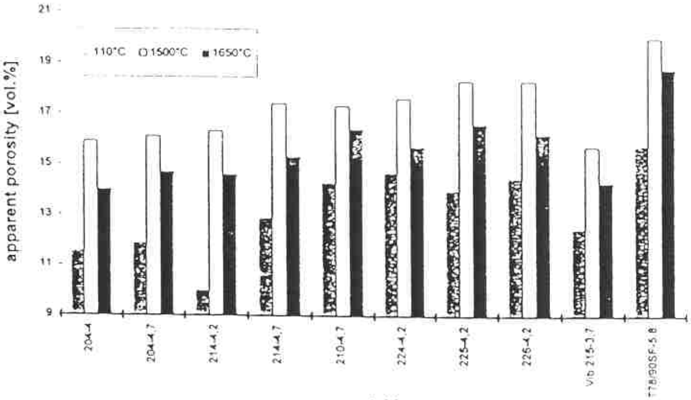

Fig. 3. Apparent porosity of selected castables

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

The P.L.C. values of all tested castables, after drying and firing up to 1500 °C, range between ± 0,1 % except the castable 210 (addition of 0,2% $Al(OH)_3$ + 0,2% Al powder) which has a P.L.C. value of – 0,22% at 1500 °C. The firing temperature of 1650 °C resulted in relatively low P.L.C. values in the range of –0,4 to –0,6%.

4.2 Bulk density and apparent porosity (Fig. 3)

Bulk density and apparent porosity with the dried and at 1500 °C and 1650 °C/5h fired samples were determined by the water immersion method. Because of the danger of rehydration, the apparent porosity cannot be determined by water absorption with the samples fired at 800 °C and 1000 °C. The results of pore size distribution by Hg intrusion (see 4.3) show an apparent porosity of the 1000 °C fired samples of 1 – 3% higher than the 110 °C dried state.

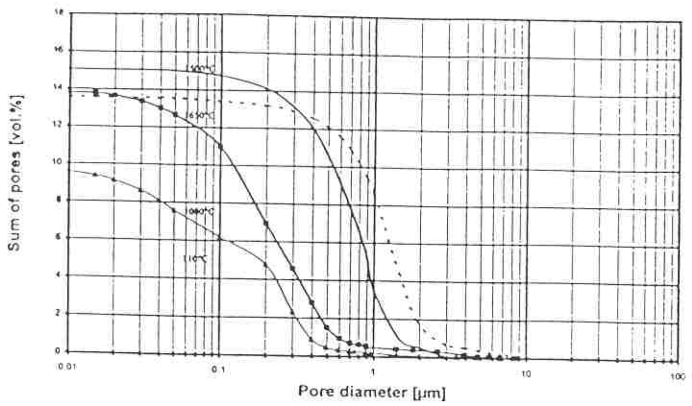

Fig. 4a. Pore size distribution of 204, 4,0% H2O at different prefiring temperatures

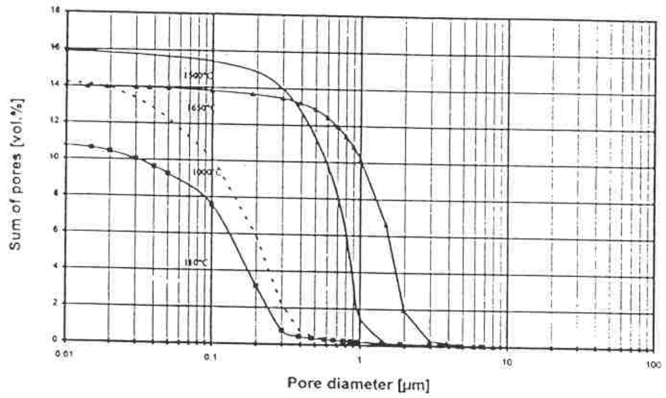

Fig. 4b. Pore size distribution of 214, 4,2% H2O at different prefiring temperatures

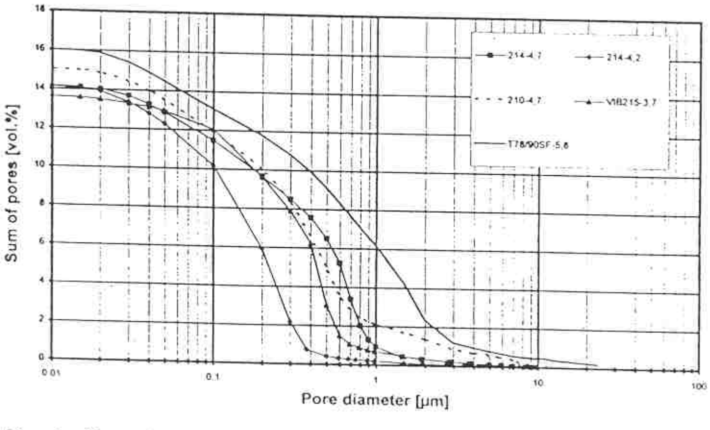

Fig. 4c. Pore size distribution of selected castables after 1000 °C prefiring

The new developed Tabular Alumina based selfleveling castables reach, after firing at 1500 °C, a not yet reported low apparent porosity between 16 – 18 vol%, and at a firing temperature of 1650 °C, between 14 – 16,5 vol%. The Spinel containing castables tend to have a higher apparent porosity compared to the pure Tabular Alumina castables.

4.3 Pore size distribution of castable 204 and 224 after different pre-firing temperatures (Fig. 4a – c)

Fig. 4a and 4b characterise the pore size distribution (Hg intrusion method), and the development of pore size, on firing up to 1650 °C of the Tabular Alumina castable 204 and the Tabular Alumina-Spinel castable 214 with low mixing water. Both selfleveling castables behave very similar and show, after firing at 1000 °C, a very low mean pore diameter of about 0,2µm. Even after firing at 1650 °C the pore diameters stay below 10µm.

Fig. 4c compares the pore size distribution after firing at 1000 °C of the new developed selfleveling castables to the conventional selfflow castable T78/90SF, which shows pore sizes above 10µm. As expected the addition of Al powder, as a drying aid, results in pore sizes between 1 and 20µm being detected in castable 210. The fine pore structure of the new developed castables guarantee a high resistance to slag infiltration.

4.4 Cold modulus of rupture (MOR) and cold crushing strength (CCS) (Fig. 5a – b)

The Fig. 5a and 5b show the development of cold strength from the cured state up to firing to 1650 °C. Compared to the conventional selfflow castable, T78/90SF, the cold strengths are significantly higher with the new selfleveling castables. Only a slight decrease in strength after firing at 1000 °C is observed. After firing at 1500 °C, and especially at 1650 °C, exceptionally high strengths are achieved. Cold crushing strength reaches above 300 N/mm^2, and modulus of rupture above 60 N/mm^2.

4.5 H.M.O.R. of selected castables at 1500 °C (Fig. 6a+6b)

The Hot Modulus of Rupture was measured on test pieces prefired at 1500 °C/5h with a soaking time of 1h before testing. The results are shown in Fig. 6a. Compared to the conventional selfflow castable, and to the H.M.O.R. values published in (1), a remarkable increase of hot strength can be stated. The highest H.M.O.R. value of 32,7 N/mm$_2$ is reached with the vibration castable 215 with mixing water of 3,7%. In case of castable 210 when Al-powder was used, the higher porosity leads to lower H.M.O.R.. Fig. 6b shows the relationship between apparent porosity of the 1500 °C prefired test pieces and their H.M.O.R. at 1500 °C. A Tabu-

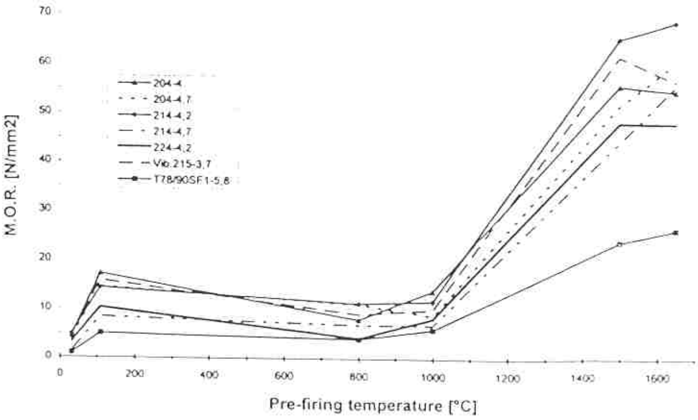

Fig. 5a. C.M.O.R of selected castables

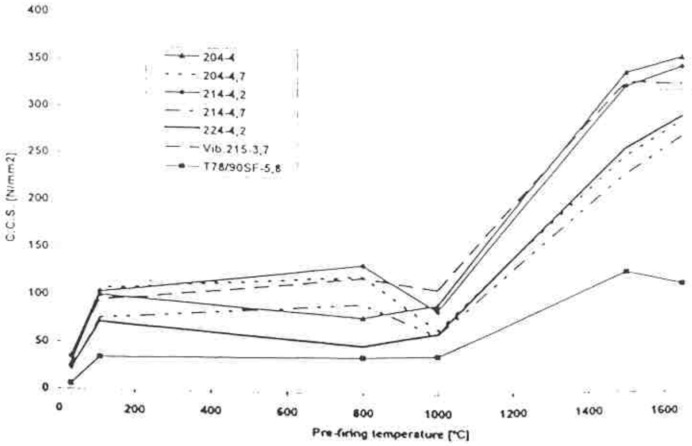

Fig. 5b. C.C.S. of selected castables

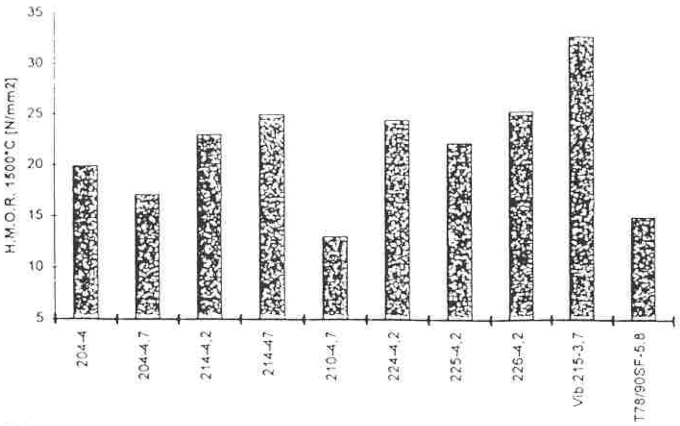

Fig. 6a. Hot modulus of rupture (1500 °C) of selected castables

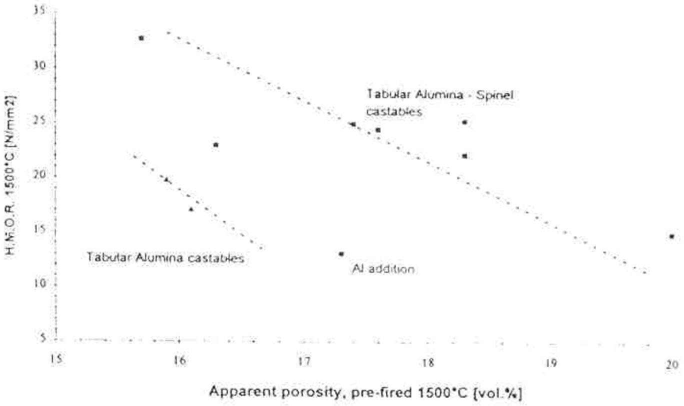

Fig. 6b. H.M.O.R. at 1500 °C as a function of apparent porosity of selected castables

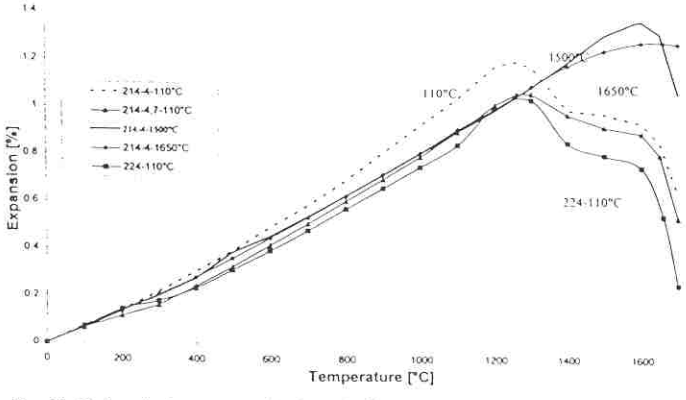

Fig. 7. Refractorieness under Load of castable 214 and 224 after different pre-firing temperatures

lar Alumina-Spinel castable develops a higher hot strength than the pure Tabular Alumina castable with the same apparent porosity. The use of the new developed functional raw materials allow a low mixing water amount, a decreased porosity and an optimised matrix design, which results in high strength values.

4.6. Refractoriness under Load (RuL) (Fig. 7)

Fig. 7 shows as an example the RuL behavior of the new developed selfleveling castable 214. Though the amount of fines in the selfleveling mixes are higher, the RuL curves are similar to the conventional SiO_2-free castables described in (1). The testing of unfired material gives an indication of changes in the material on first heating or (sintering, formation of CA_6). After pre-firing at 1500 °C the RuL curve shows a further small reaction over 1500 °C causing a slight expansion. After pre-firing at 1650 °C the material is fully reacted and sintered showing an excellent refractoriness under load up to 1700 °C.

Tab. 6. Thermal Shock Resistance of selected castables

Castable	pre-firing temperature	cycles air quenching	loss of sonic velocity [%] after 5 cycles	after 10 cycles
204-4,7	1000 °C	> 10	49	54
204-4,0		> 10	47	52
214-4,2		> 10	45	52
204-4,7	1500 °C	3-4		
204-4,0		2		
216-4,6	1650 °C	2-4		

4.7 Thermal shock resistance

The air quenching method, according to DIN 51 068, was used to characterise (in a practical manner) the resistance to thermal shock of the new developed selfleveling castable **(Tab. 6).** If prefired at 1000 °C, a temperature to which for instance monolithic lined ladles are pre-heated, the selfleveling castables show a good thermal shock resistance with > 10 cycles. When firing at higher temperatures it is clear, that as a result of the formation of a low porosity, corrosion resistant structure the thermal shock resistance can only be low.

4.8 Corrosion resistance

The new selfleveling castables 224 (#2 in **Fig. 8**), 225 (# 3) and 226 (# 4) where tested, together with the conventional selfflowing castable T78/90SF (#1), in an induction furnace at 1650 °C for 6h using a basic slag (Fe- and Mn-rich, C/S=2,0) and steel ST 37. In castable 224 the lowest corrosion depth of only 8 mm was found, compared to 10 mm of the other materials. All castables showed almost no penetration. The corrosion mechanism in case of the used slag is obvious dominated by chemical dissolution.

5. Placement properties

For evaluating the placement properties of the newly developed selfleveling castables the following characteristics have been determined:

- flowability as a function of time at different temperatures (flow cone test)
- curing strength development as a function of time and curing temperature
- exothermic reaction of the castable during curing as function of curing temperature

To simulate different seasonal and regional conditions, the tests were conducted at 7 °C, 15 °C, 20 °C and 35 °C.

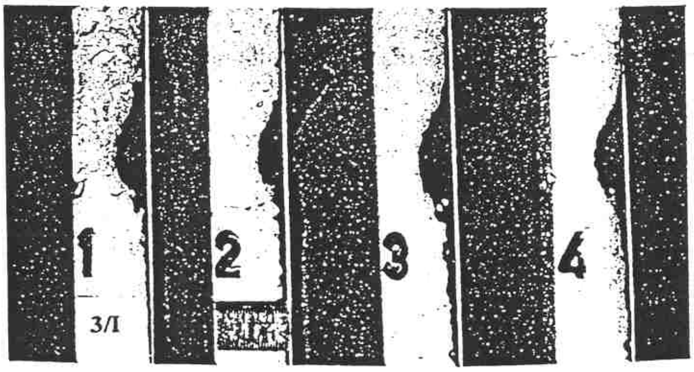

Fig. 8: Corrosion resistance of the spind-rich selfleveling castables 224 (2), 225 (3) and 226 (4) compared to the conventional selfflowing castable T78/90 SF (1)

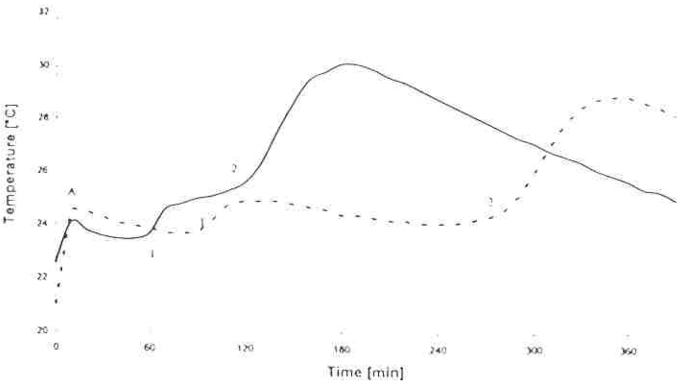

Fig. 9. Exothermic test

Test description:

For all testing, 5kg batches dry mixed for 1 min and wet mixed for 4 minutes were used. The batch is separated into 2 parts and put in plastic containers. One container for the exothermic reaction and one for the self flow test.

The exothermic reaction test:

The castable is cast into a container without compacting or vibration. A sensitive thermocouple (type J) is put into the castable and connected to a measurement device. The castable is covered to prevent drying. The temperature of the mix is measured as function of time until complete hydration.

The self flow cone test: As described in Fig. 2, chapter 3

Testing at different temperatures:

The tests performed by 20 °C were done in a lab with an ambient temperature of 20 °C ± 1 °C. For the other temperatures a climate cabinet, which contained all required materials and test equipment, was used. Mixing was done outside the climate cabinet, with temperature adjusted equipment, in addition the self flow tests at the different measurement times were performed outside the cabinet. For the self flow test a temperature adjusted 1cm thick metal plate was used which allows a consistent temperature during the flow test to be maintained. After each measurement the castable and the necessary equipment are put back in the climate cabinet to ensure that the constant temperature is maintained. For all testing the flow is followed until a condition of no flow is observed.

The two diagrams in **Fig. 9** graphically depict the measured exothermic reaction curves. There are 3 principle areas of temperature changes.

As a result of the mixing energy, the temperature rises in the beginning (indicated as A in Fig. 9), after mixing stops the temperature returns to the ambient temperature. After a period of relative temperature stability there is a small temperature increase, indicating an exothermic reaction (1 in Fig. 9). The time this first temperature increase occurs correlates directly with the end of selfflowability of the castable. The mix becomes stiff but does not have any demolding strength. A third area of temperature increase (point 2 in Fig. 9) results from full cement hydration and indicates the time when the castable develops mechanical strength. The time at which the maximum temperature is reached is recorded as t_{Tmax}.

The compositions 204 (Tabular Alumina) and 214 (Tabular Alumina-Spinel) (see Tab. 3a) were selected to study the effect of the dispersing Aluminas, ADS 1 and ADW 1, and the influence of different placement temperatures and water content on selfflowing time and hardening. Some selected characteristic results are shown.

Tab. 7a. Flowability of castables 204 and 214 at different temperatures

Castable	204			214		
Test temp. [°C]	7	20	35	7	20	35
ADS 1 [%]	0	0,5	1,0	0	0,5	1,0
ADW 1 [%]	1,0	0,5	0	1,0	0,5	0
Mixing H_2O [%]	4,2	4,2	4,2	4,2	4,2	4,2
Flow diameter after 10 min [cm]	21,7	24,3	24,5	19,0	23,0	22,0
30 min [cm]	21,4	24,5	23,0	19,7	22,7	20,5
60 min [cm]	21,1	23,5	no flow	18,7	22,3	no flow
90 min [cm]	20,7	no flow		18,5	no flow	
120 min [cm]	21,0			18,5		
150 min [cm]	no flow		no flow			
Exo curve first reaction [min]	223	72	51	241	83	46
Time of t_{Tmax} [min]	622	204	161	636	269	314

1) All test species cured at the test temperatures

Tab. 7b. Early strength development during curing at different temperature levels of castables 204, 214 and 224

Castable	214	214	214	214	214	204	204	204	224
H2O [%]	4,7	4,7	4,7	4,7	4,2	4,2	4,2	4,2	4,2
Temp. [oc]	7	15	20	35	35	20	20	35	20
ADS 1 [%]	0	0,5	0,5	1,0	1,0	0,5	1,0	1,0	0,5
ADW1 [%]	1,0	0,5	0,5	0	0	0,5	0	0	0,5
CCS [N/mm^2]									
3h	n.d.	n.d.	n.d.	n.d.	n.d.	5,6	0	n.d.	n.d.
4h	n.d.	n.d.	n.d.	n.d.	n.d.	9,4	0	n.d.	7,3
6h	6,3	5,6	10,6	15,6	23,1	15,6	2,5	29,4	9,7
12h	20,0	20,6	16,9	15,0	28,8	22,5	10,3	30,6	15,6
24h	28,8	29,4	18,8	24,4	31,9	22,5	n.d.	32,5	n.d.
CMOR [N/mm^2]									
3h	n.d.	n.d.	n.d.	n.d.	n.d.	0,9	0	n.d.	n.d.
4h	n.d.	n.d.	n.d.	n.d.	n.d.	1,8	0	n.d.	0,6
6h	0,5	0,5	1,2	1,6	3,3	3,2	0	5,6	1,3
12h	4,2	3,3	2,8	2,1	4,2	4,7	0	6,1	3,8
24h	5,6	4,7	3,4	2,8	5,2	4,7	0	6,1	n.d.

5.1 Temperature influence on castable flowability time and curing strength development

In **Tab. 7a** the flowability of castables 204 and 214 at 7 °C, 20 °C and 35 °C are shown. To adjust the castable to the different temperatures, different addition of ADS 1 and ADW 1 have been used as indicated in the table. Both castables show, even at 35 °C, 30 min of consistent high selfflowability. At 7 °C flowability is achieved for 120 min. The development of the cured strength of castable 214 **(Tab. 7b)** clearly indicates that even at 7 °C placement and curing temperature setting is not delayed considerably. The results of the exotherm test with castable 204 are shown in **Fig. 10.**

5.2 Flowability as a function of the mixing water content

Tab. 8 lists the selfflowability of castable 204. Where 4,2 % water seems to be the optimum addition, 4,7 % water can be considered as maximum, 4,0 % water is the minimum for obtaining accepta-

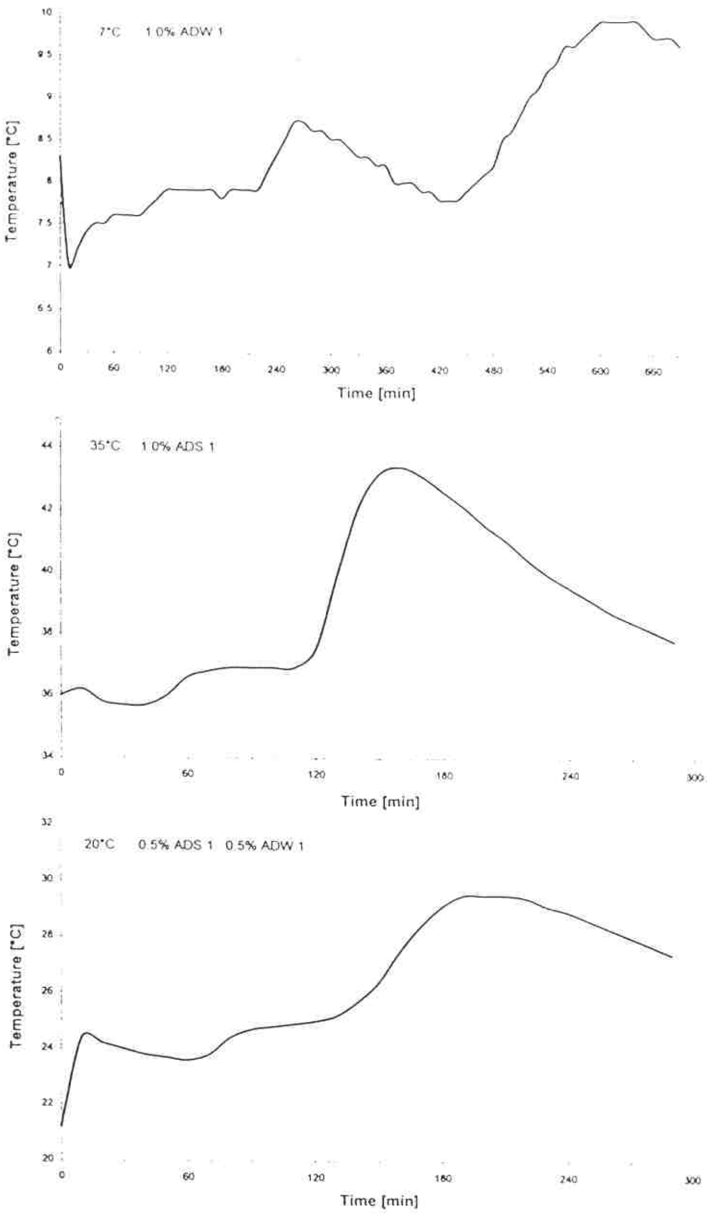

Fig. 10. Exotherm test at 7 °C, 20 °C and 35 °C of castable 204 with mixing water of 4,2%

ble selfflow properties. The result of the exotherm test **(Fig. 11)** indicates only little influence of the mixing water on setting time.

5.3 Control of the flowability time

In **Fig. 12** and **Tab. 9**, the influence of different concentrations of ADS 1 and ADW 1 is demonstrated. By a slight change of the ADS 1/ ADW 1 component by 0,25%, the flowability can either be extended from 60 to 90 min or reduced to 30 min.

5.4 Influence of Microsilica

To investigate if the addition of superfine particles like Microsilica can further reduce H_2O demand and increase flowability, 1% and 2% of Microsilica was added to castable 204. Surprisingly it was found that Microsilica not only decreased the flowability in the investigated castables but destroyed selfflow totally when added in a concentration of 2%. Even 1% reduced selfflow from 24,3 to 19,5 cm **(Tab. 10)**. Furthermore the exothermic reaction of the castable was delayed substantially when 2% Microsilica **(Fig. 13)**, in combination with 1% ADS 1 is used in castable 204, was added.

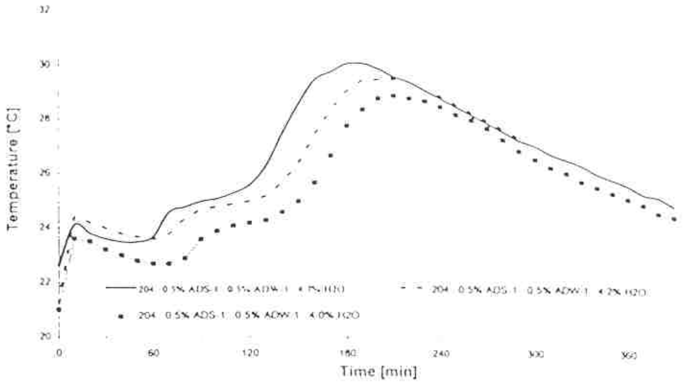

Fig. 11. Influence of mixing water content on exothermic test curve

5.5 Influence of cement reactivity

9 different lots of cement have been tested in castable 204 on flowability and exothermic reactivity **(Tab. 11)**. The tested cement lots varied when tested in age between 1 day after production (lot 8,9) and 6 months (lot 1). The results show a very high consistency in selfflowing varying only between 24,2 – 25 cm after 10 min and 23 – 25 cm after 30 min. The time necessary to reach the maximum temperature in the exotherm test varies between 150 and 204 min, which indicates a consistent and reproducable setting behavior of all lots.

Tab. 8. Flowability and mixing water content of castable 204

Castable	204			
Test temp. [°C]	20			
ADS 1 [%]	0,5			
ADW 1 [%]	0,5			
H2O [%]	4,7	4,2	4,0	3,7
Flow diameter after 10 min [cm]	28,5	24,3	20,0	no flow
30 min [cm]	28,0	24,5	20,5	
60 min [cm]	27,2	23,5	19,8	
90 min [cm]	no flow	no flow	no flow	

Tab. 9. Flowability and concentration of the dispersing alumina 5

Castable	204		
Testtemp. [°C]	20		
ADS 1 [%]	0,5	0,25	0,75
ADW 1 [°/0]	0,5	0,75	0,25
H_2O [%]	4,7	4,7	4,7
Flow diameter after 10 min [cm]	28,5	29,0	30,0
30 min [cm]	28,0	28,0	29,0
45 min [cm]	–	no flow	–
60 min [cm]	27,2		29,5
90 min [cm]	no flow		27,0
120 min [cm]			no flow
t_{Tmax} [min]	186	122	356

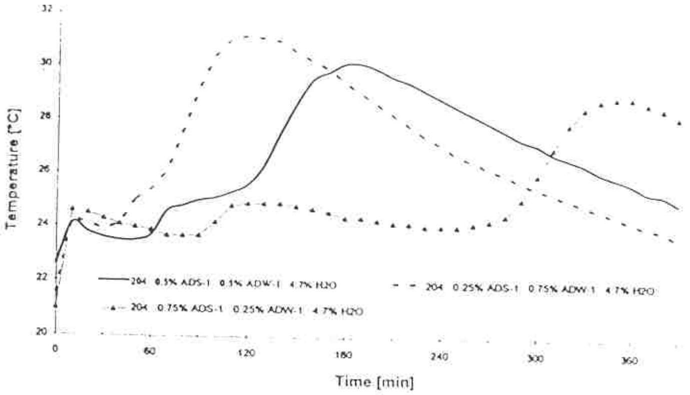

Fig. 12. Influence of different concentration of dispersing aluminas on exothermic test curve

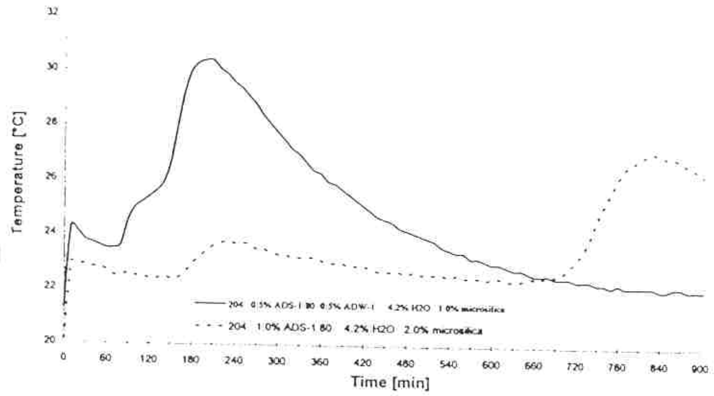

Fig. 13. Influence of microsilica on the exothermic reactions

6. Conclusion

The newly developed **Matrix Advantage System** allows the development of Microsilica-free low cement Tabular Alumina and low cement Tabular Alumina-Spinel castables requiring only 4,0 – 4,2% water additions to achieve full selfleveling performance. This compares with conventional low cement castables which need typically 5,7 – 5,9% for selfleveling, representing a water reduction of almost 30%. This decrease in mixing water results in low open porosity and exceptional mechanical strength in both dried and fired samples. Again it was proven that the addition of alumina-rich Spinel significantly increases the H.M.O.R. at 1500 °C. Strength values over 20 N/mm^2 up to 33 N/mm^2 can be easily achieved.

More remarkable is the good high-temperature-volume-stability of the developed castables, despite their high content of fine and superfine particles. Even at 1650 °C a firing shrinkage of only 0,4 to 0,6% has been observed.

It has been demonstrated that the new Matrix System is also suitable for vibration castables. Even a higher hot strength and lower porosity than in selfleveling castables can be achieved.

The specific properties of the dispersing Aluminas ADS 1 and ADW 1 allows the controlled adjustment of flowability and demolding time to meet the different requirements resulting from different climate, applications and equipment. This enables the refractory producer to fine tune his castables to the various needs.

Tab. 10. Influence of Microsilica on flowability

Castable	204		
Test temp. [°C]	20		
ADS 1 [%]	0,5	0,5	1,0
ADW 1 [%]	0,5	0,5	–
Microsilica [%]	0	1,0	2,0
H_2O [%]	4,2	4,2	4,2
Flow diameter after 10 min [cm]	24,3	19,5	No flow
30 min [cm]	24,5	20,5	consistency is wet, but stiff
60 min [cm]	23,5	19,5	
90 min [cm]	no flow	no flow	
t_{Tmax} [min]	204	207	831

Tab. 11. Flowability and reactivity of castable 204 with different cement lots

Castable	204								
Test temp. [°C]	20								
Cement lot	1	2	3	4	5	6	7	8	9
ADS 1 [%]	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5
ADW 1 [%]	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5	0,5
H20 [%]	4,2	4,2	4,2	4,2	4,2	4,2	4,2	4,2	4,2
Flow diameter 10 min [cm]	24,3	25,0	24,3	24,7	25,0	24,3	24,2	24,8	24,3
30 min [cm]	24,5	24,0	25,0	24,6	24,5	24,5	24,0	23,0	23,8
60 min [cm]	23,5	no flow	14,5	no flow	no flow	no flow	no flow	no flow	no flow
90 min [cm]	no flow		no flow						
t_{Tmax} [min]	204	151	172	171	169	177	193	152	150

References

[1] *Kriechbaum, G. W.; Gnauck, V.; Routschka, G.:* The influence of SiO_2 and Spinel on the hot properties of high Alumina low cement castables. Stahl u. Eisen Special – XXXVIIth International Colloquium on Refractories, Aachen, Oct. 1994, S. 150 – 159

[2] *Yamamura, T.; Kaneshige, T.; Miyawaki, T. u.a.:* Development of self-flow type Alumina-Spinel castable Refractories. Shinagawa Techn. Rep. (1994) H. 37, 39 – 54

[3] *Bugajski, M.; Schwaiger, R.:* Freifließende Gießmassen – eine neue Generation ungeformter feuerfester Produkte. Veitsch-Radex Rundschau (1996)1, 44 – 52

[4] *Zografou, C.; Hatzigiuvanis, H. u.a.:* Untersuchungen zur feuerfesten Zustellung von modernen Hochleistungs-MF-Induktionstiegelöfen mit mikroporösen Feuerbetonen auf Al_2O_3/Spinell-Basis. XXXVIII. Int. Feuerfestkolloquium, Feuerfeste Werkstoffe für Giessereien. Aachen 1995, S. 40 – 47

[5] *MacZura, G.; Madono, M.; Kriechbaum, G.W. u.a.:* Low moisture regular corundum (Spinel castable with superior properties) in: UNITECR'95 congress proceedings, Vol. 3 (1995) S. 179 – 186

[6] *Ymamura, T.; Sumimura, H.; Tanigawa, S.:* Effects of curing temperature on hardening and properties of low cement castables. Shinagawa Techn. Rep. (1995) H. 38, 11 – 21

[7] *Mori, J. u.a.:* Structure change of alumina castable by addition of magnesia or spinel. Taikabutsu Overseas 15 (1995)3, 20 – 23

[8] *Nakashima, H. u.a.:* Application of self-flow type castable refractories. in: UNITECR'95 congress proceedings, Vol. 2 (1995) S. 205 – 213

[9] *Hamazaki, Y. u.a.:* Mineral composition change matrix of alumina-spinel castable. Shinagawa Techn. Rep. (1996) H. 39, 45 – 56