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# Castables for kiln furniture

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*The fine art of*



# CASTABLES FOR KILN FURNITURE

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## Abstract

Mullite is widely known as a highly creep resistant refractory phase. In the development of low cement and ultra low cement microsilica containing castables, the mullite formation in the bond system has been of major importance in improving the refractoriness. In this work mullite bonded castables will be evaluated as candidate materials for kiln furniture. Both fused alumina and SiC based materials will be investigated.

## Introduction

Kiln furniture are traditionally manufactured by pressing. To-day other ceramic forming methods are frequently used, especially in production of more advanced ceramic kiln furniture, e.g. recrystallized SiC (R-SiC) and silicon-infiltrated reaction bonded SiC (SiSiC).<sup>1</sup> Production of kiln furniture from refractory castables should possess several advantages compared to conventional pressing. Refractory castables generally have low shrinkage during production, which is considered especially important when manufacturing large shapes.<sup>1</sup> There should be little restriction on shapes since refractory castable are readily cast into complex shapes.

High thermal shock resistance, high creep resistance and good mechanical strength at high temperature are essential material properties for good kiln furniture.

In this work mullite bonded castables will be investigated since mullite as a bonding phase exhibits high refractoriness, low creep rate, low thermal expansion, good stability and strength.<sup>2</sup>

Silicon carbide ceramics has extraordinarily high thermal shock resistance, high strength and high-temperature creep stability, making them very suitable for kiln furniture.<sup>1</sup> In the present work the excellent properties of SiC and mullite will be combined in a mullite bonded SiC castable.

Refractory castables are a very diversified group of material, covering conventional castables, low cement, ultra low cement and recently the no-cement castables. In this work mullite bonded low cement and ultra low cement castables based on fused alumina aggregates will be examined.

## Experimental procedure

For this investigation the composition of the castables followed the Andreassen distribution\* with distribution coefficient, q-value = 0.25-0.26.<sup>3</sup> White fused alumina with top size 4 mm was chosen together with calcined alumina and super fines in four of the total five castables, see Table 1. In the three ultra low cement castables labeled CA 0.5, the microsilica was gradually substituted by reactive alumina in fractions of volume. This was done for 0, 50 and 100% (volume) substitution according to the labels 100/0, 50/50 and 0/100. In the low cement alumina based castables (CA 6, 100/0), only microsilica was used in the superfine fraction (submicron). SiC aggregates with top size 2 mm was used in the silicon carbide based castable (CA 0.5, SiC), see Table 2. The bond phase composition was quite similar to the fused alumina based castables. The intention was to design a mullite forming ultra low cement SiC castable.

### *Sample preparation*

The castables were dry mixed for 4 minutes and subsequently added 13 volume percent water and mixed for another 4 minutes. Flow measurements were performed using the flow cone described in the ASTM C230 procedure. Samples were cast and cured for 24 hours before drying at 110°C.

Density and porosity were determined by the liquid immersion method. Hot modulus of rupture was measured according to the PRE R18 standard procedure. The samples were placed in the furnace and heated to the test temperature at a heating rate of 300°C/hr. The samples were pre-fired at the testing temperature for a predetermined time before measuring the hot modulus of rupture (hot M.O.R)

The samples (height = diameter = 50 mm) used for refractoriness under load (RUL) measurements (pre-fired at 1000°C/12 hours), were prepared from bricks. RUL was measured according to the ISO 3187 procedure. The samples were heated at 300°C/hr to the maximum test temperature (1600°C) using a constant compressive stress of 0.2 MPa. The samples were kept at 1600°C for 25 hours under constant load (0.2 MPa)

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\* CPFT (vol%) =  $(d/D)^q$

CPFT = Cumulative Percentage Finer Than

D = max. particle size

d = particle size

q = distribution coefficient

Table 1: Ultra low cement and low cement castables based on fused alumina. Top size 4 mm and  $q=0.25$ .

Ratio MS <sup>†</sup> /Al <sub>2</sub> O <sub>3</sub> <sup>‡</sup> (vol%)	CA 0.5 100/0	CA 0.5 50/50	CA 0.5 0/100	CA 6 100/0
<i>Components (wt%)</i>				
White fused alumina:				
2-4 mm	10	9,5	9,5	10
0,5-3 mm	32	31	30	32
0-0,4 mm	22	21	20,5	22
< 74 micron	20	19,5	19	15
Cement §	0,5	0,5	0,5	6
Alphabond 200 (hydraulic alumina)	0,5	0,5	0,5	0
Microsilica (983 U)	8	4	0	8
CT3000SG (superground alumina)	0	7	13,5	0
HVA SG (calcined alumina)	7	7	6,5	7
Citric acid (retarder)	0	0	0,03	0
Darvan 811D (deflocculant)	0,05	0,05	0,05	0,05
Water (13 vol%)	4,10	3,97	3,85	4,15

Table 2 Ultra low cement castable based on silicon carbide. Top size 2 mm and  $q= 0.26$ .

	CA 0.5 SiC
<i>Components (wt%):</i>	
SiC 8/14 (Norton)	30
SiC 24/120 (Norton)	35,5
White fused alumina < 74 micron	16,5
Baco MA 95 (calcined alumina)	9
Alphabond 200 (hydraulic alumina)	0,5
CA-26	0,5
Microsilica (983 U)	8
Darvan 811D (deflocculant)	0,05
Water (13 vol%)	4,0

<sup>†</sup> Elkem Microsilica 983 U

<sup>‡</sup> Reactive alumina CT3000 SG (ALCOA)

<sup>§</sup> CA-14C in castables with 0.5 wt% cement and CA-26 in castables with 6 wt% cement.

## Results and discussion

Figure 1 shows the flow values immediately after mixing. Addition of reactive alumina reduce the flow both in the ultra low cement and low cement castables. The reason for this is not fully understood, but may be connected to shape and narrow particle size distribution of the reactive alumina. Problems connected to deflocculation may also contribute. Whether the system contains 0.5 or 6 wt% cement does not seem to be of major importance as long as the system is well retarded. Neither seem the change of aggregates from white fused alumina to SiC to influence flow significantly. This is probably true as long as the aggregates are dense with very little/no open porosity. Low flow value can often be improved by adding more water, however more water increase the porosity of the final product. Higher porosity gives lower mechanical and thermo-mechanical properties.

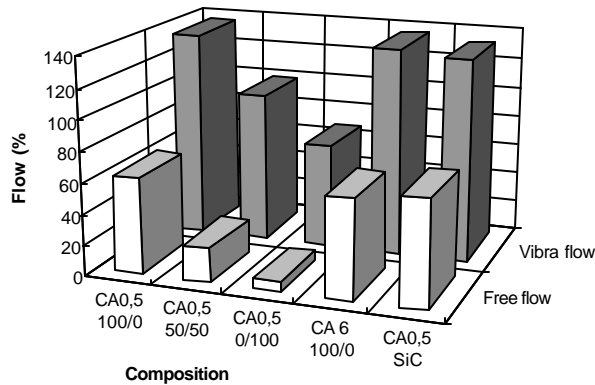


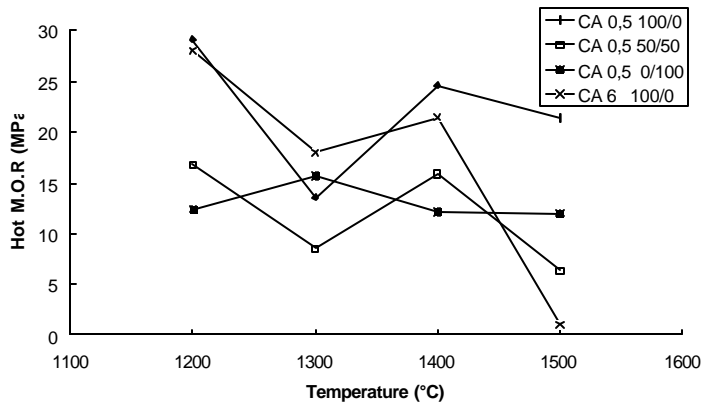
Figure 1 Free flow and vibra flow of the castables in Table 1 and Table 2. 13 vol% water.

The thermo-mechanical properties are important features for kiln furniture due to their function as load bearing elements. Hence, the materials were characterized by testing hot modulus of rupture (Hot M.O.R.) and refractoriness under load. Hot M.O.R was tested after 24 hours of pre-firing and the results are given in Figure 2. The hot M.O.R. of the ultra low cement castables is influenced by the substitution of reactive alumina for the microsilica in the super fine fraction. Mullite formation above 1300°C gives improved strength for the microsilica containing castables. However, the less SiO<sub>2</sub> available in the sample (CA 0.5, 50/50) compared to the (CA 0.5 100/0), gives less mullite formation and hence lower strength at 1400 and 1500°C. The ULCC with 100 volume% substitution of microsilica (0/100) is almost a pure alumina castables (Al<sub>2</sub>O<sub>3</sub> >99.8 wt%), hence formation of mullite is absent and the hot M.O.R. is primarily due to sintering of the alumina fines. The dip in strength generally observed at 1300°C for fused alumina samples containing microsilica, is attributed to formation of a liquid phase. Traditionally, liquid phase formation in similar systems has been attributed to impurities, mainly CaO from the

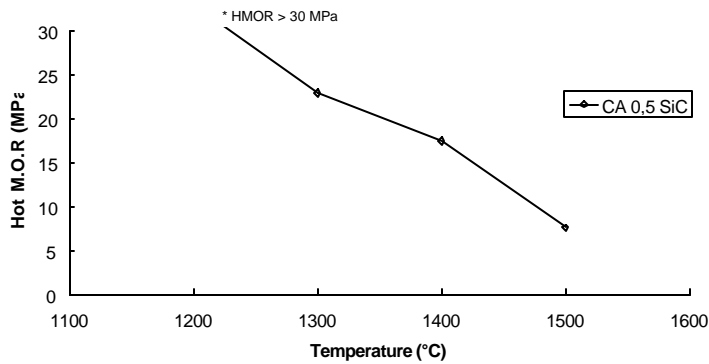
cement. However, the total lime content is below 0.2 wt% in the ULC-castables containing only 0.5 wt% cement. It is therefore considered unlikely that lime could cause the observed effect at 1300°C. In a previous paper,<sup>4</sup> liquid formation with subsequent mullite precipitation was discussed using information from a phase diagram on the meta-stable system alumina-silica published by Risbud and Pask.<sup>5</sup> There is observed a eutectic at 1260°C in the alumina-silica system. It is then tempting to connect the phase diagram and the observed hot strength data and conclude that not only impurities cause liquid formation around 1300°C, but also the inherent characteristics of the phase diagram.

The hot M.O.R of the low cement castables (CA 6, 100/0) are given in Figure 2a. The hot M.O.R. is rather high in the interval 1200-1400°C. Again there is observed a dip in strength at 1300°C, however this time the lime content is much higher (6 wt% cement) and lime of course contributes more to the liquid formation. Mullite precipitation gives rise to increased strength at 1400°C, however at 1500°C excessive amounts of liquid is formed and the sample lose its hot flexural strength quite drastically.

The silicon carbide based castable does not show the same pattern in hot M.O.R. as the corresponding mullite bonded fused alumina castables, see Figure 2b. The SiC-castable exhibits very high hot strength up to 1300°C. At higher temperatures, although mullite was observed (by XRD analysis), the strength rapidly decreased, without the characteristic dip and increase. This is probably due to beginning oxidation of the SiC aggregates.



a)



b)

Figure 2 Hot modulus of rupture after 24 hours at test temperature, a) fused alumina based castables and b) silicon carbide based castable.

The creep behavior of the refractory materials were investigated by measuring refractoriness under load (RUL). The results are given in Figure 3. The left part of the curves represents the thermal expansion during heat up at 300°C/hr under constant load. The right hand part of the figure represents a creep curve under constant conditions of stress and temperature, i.e. 0.2 MPa and 1600°C.

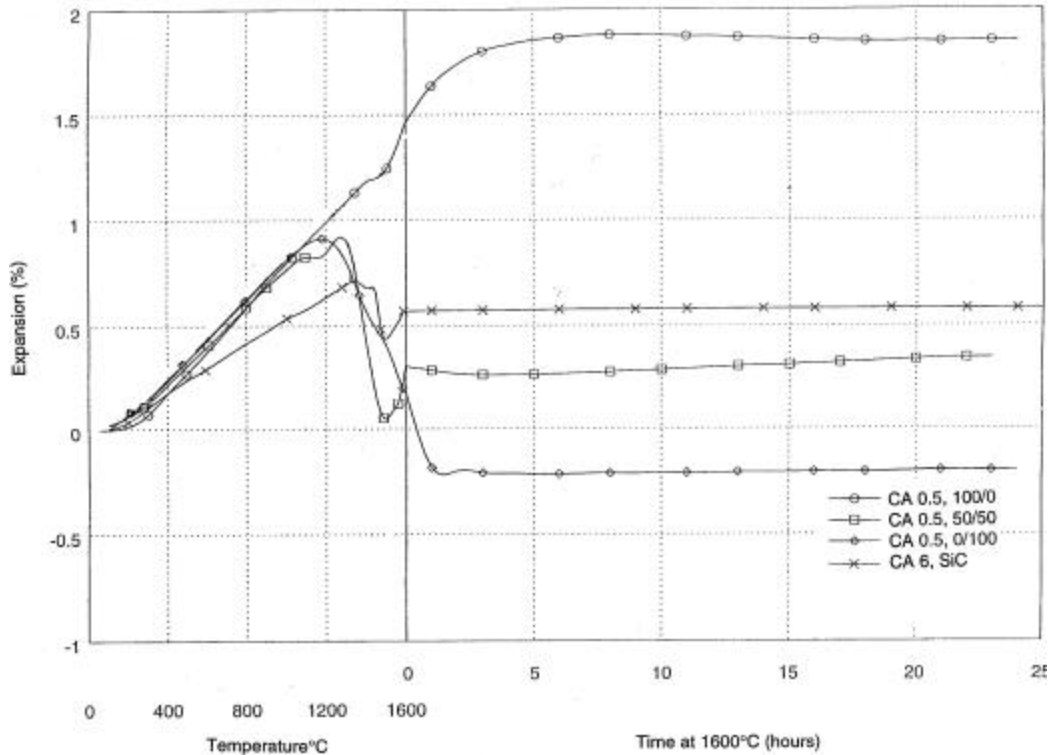


Figure 3 Refractoriness under load measurements.

The ULC castables expand linearly up to between 1200-1400°C. The sample (CA 0.5,100/0) exhibits a small plateau around 1400°C and then the expansion continues up to 1600°C, probably as a consequence of mullite formation. The expansion even continues for a while under the constant condition at 1600°C. Partly substitution of reactive alumina for microsilica in the sample (CA 0.5, 50/50), resulted in a relatively large compression around 1300°C followed by expansion above 1450-1500°C. The relatively large compression is believed being caused by formation of the meta-stable liquid phase in the system  $\text{Al}_2\text{O}_3\text{-SiO}_2$ . The absence of compression in the sample (CA 0,5, 100/0) is not fully understood, but more available  $\text{SiO}_2$  might give more rapid mullite formation and increased viscosity of the meta-stable liquid. Under stable condition at 1600°C both ULC-samples containing microsilica show good creep resistance.

The sample (CA 0.5, 0/100), with microsilica fully replaced by alumina, shows a large compression between 1200-1600°C. This shrinkage is probably caused by sintering of the superfine and reactive alumina. The sample gained high creep resistance at 1600°C.

The mullite bonded ultra low cement alumina based castables showed remarkably good creep resistance at steady conditions at 1600°C. Hence, the mullite bonded alumina based ULCC seem to be promising materials for kiln furniture. Zhang et

al.<sup>6</sup> observed that microsilica has a beneficial influence on the creep resistance in no-cement high alumina castables due to the formation mullite in the matrix. It is however, worth noticing that Zhang et al.<sup>6</sup> always observed some creep at steady conditions at 1600°C. The differences in creep resistance are probably due to differences e.g. in the mix designs and experimental conditions. Zhang et al.<sup>6</sup> varies among others, the content of hydraulic alumina from 2-7 wt%.

The permanent linear change at 1400°C was 0.5 % for the sample (CA 0.5, 100/0). The expansion due to mullite formation will only occur during the pre-firing procedure in the manufacturing process as shown by Zhang et al.<sup>6</sup> However, this can be reduce to 0.1 wt% by replacing 4 wt% of the calcined alumina (< 74 µm) with 4 wt% raw kyanite.<sup>4</sup>

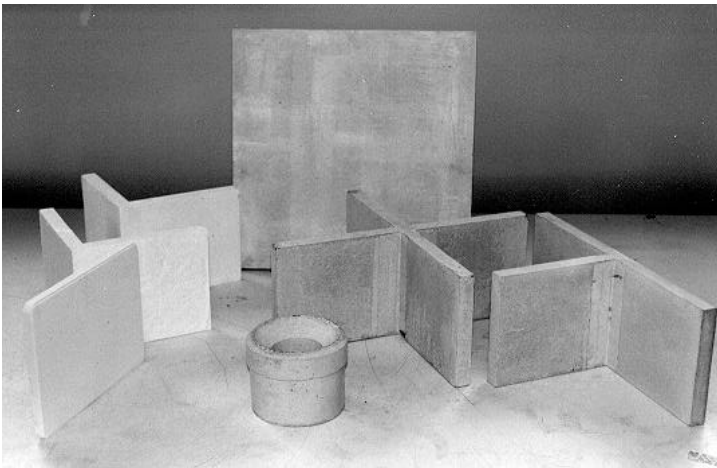
The low cement castable containing microsilica and cement are not suitable at 1600°C due to heavy liquid formation. The castable substituted by alumina however, were tested. The expansion above 1300°C is probably due to formation of the phase CA<sub>6</sub>. Also this sample gain high creep resistance at 1600°C.

The mullite bonded SiC castable was tested at 1600°C. The inherent thermal expansion of SiC is lower than that of alumina. The SiC castable was compressed to some degree (0.2-0.25 %) around 1300-1400°C. The compression was followed by expansion. This creep “pattern” is very similar to the creep observed for the alumina based materials, excepted for the lower total expansions. Hence, the observed effect is probably caused by liquid formation followed by mullite precipitation. The SiC castable revealed very high creep resistance at 1600°C. According to the RUL results and the hot M.O.R measurements, mullite bonded SiC castable seem a promising material for kiln furniture. However, high temperature oxidation of SiC limits its high temperature service life. Oxidation of SiC will take place throughout the whole cross section of the castable due to the open porosity (approximately 12 vol%). High temperature oxidation mechanism of recrystallised SiC (R-SiC) with similar porosity, has been described by A. Sonntag.<sup>1</sup> The oxidation of SiC can be “delayed” by coating the surface with a Al<sub>2</sub>O<sub>3</sub> layer.<sup>7</sup> Such coating will extend the life time of the mullite bonded castable at temperatures above 1300°C.

Examples of casted kiln furniture based on the mixes in Table 1 and 2 are given in Figure 4.



a)



b)

Figure 4 Mullite bonded kiln furniture. a) Alumina based ultra low cement castable (CA 0.5, 100/0) and b) selection of shapes of the castables (CA 0.5, 100/0) and (CA 0.5, SiC).

## Conclusions

Low cement (LC) and ultra low cement (ULC) castables has been investigated for use as kiln furniture. The LC castable is suitable for use below 1500°C. The ULC castables show very good creep resistance at 1600°C due to mullite formation and sintering in the super fine fraction. The ULC castable based on silicon carbide aggregates needs a coating (e.g. alumina) to prevent severe oxidation above 1300°C. Microsilica generally improves flowability of castables at low water level and promotes mullite formation above 1300°C.

## References

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