

The Optimisation of Magnesia Containing Castables Containing Calcium Magnesium Aluminate Cement

J.-M. Auvray, C. Wöhrmeyer, S. Li, C. Parr, H. Fryda

Calcium magnesium aluminate (CMA) is a novel binder for steel ladle castables. It was reported previously that CMA has hydraulic properties and is beneficial in the matrix of castables to prevent ladle slag penetration and corrosion [1, 2]. The CMA grain contains microcrystalline magnesium aluminate spinel which is homogeneously distributed between hydraulic calcium aluminate phases. Applied in castables it develops an unique microspinel matrix.

This study presents further application studies of magnesia containing castables based upon CMA. Both pre-formed magnesium aluminate spinel and magnesia are combined in different model systems. The matrix spinel contained within the model castables is derived from fused spinel, sintered spinel and combined with different quantities of spinel from CMA.

At equal CaO contents CMA develops the same strength after drying but higher strength after firing is found than with a reference system of calcium aluminate cement (CAC) + spinel. This is assumed to be the effect of a higher sintering reactivity of the microspinel in CMA.

Model alumina magnesia castables can be formulated around the addition of magnesia and CMA inside the castable matrix. The magnesia addition in CMA enables a reduction of free magnesia leading to an improvement of rheological properties and reduction of cracking risk associated with brucite formation during drying. This will still deliver improved corrosion resistance relative to reference alumina magnesia castable systems. Furthermore with a reduced magnesia content a lower permanent expansion due to less in situ spinel formation had been observed [2]. The present study shows that this enables a reduction of silica and improves the thermomechanical properties. However, it was found that with CMA the quantity of silica can be reduced, but nonetheless a small silica addition is recommended inside the castable matrix as it minimises the magnesia hydration and crack formation during castable drying.

1 Introduction

Studies by *Kantani* and *Imaiida* [3] have shown that the best compromise between ladle slag penetration and corrosion resistance can be achieved when the castable contains about 20–40 % magnesium aluminate spinel after firing. The spinel can either be added as pre-reacted spinel or formed in situ by adding magnesia to the castable. Furthermore, it was discovered that the penetration resistance increases when the spinel size was reduced [4]. Very fine spinel can be created when magnesia is added to the castable. It reacts during firing with the alumina filler to form spinel in situ. The merits of the two formulation logics have been debated and discussed extensive-

ly [5] and the general view is that each system brings a specific set of material properties that can be exploited in different applications and that one system is not necessarily dominant or better than the other. In the case of the alumina magnesia castables, the magnesia addition often leads to negative side effects, for example, rheology problems and crack formation during dry-out due to the magnesia hydration and related volume expansion. Furthermore a high volume increase at high temperature occurs due to in situ spinel formation. To limit this expansion to an acceptable level small amounts of silica are often added which creates a certain amount of liquid phase during firing. That counteracts the expansion caused by the

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Keywords: castable, calcium aluminate, magnesium aluminate, spinel magnesia

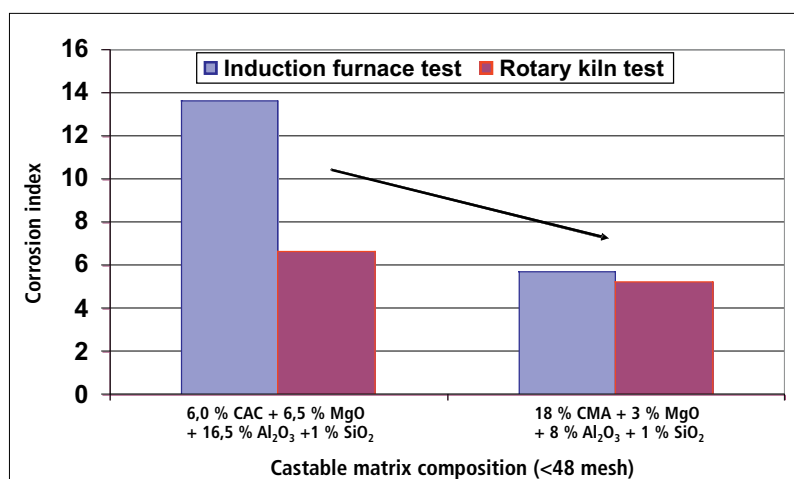


Fig. 1 Corrosion index of alumina magnesia castable with CAC and CMA. Slag: C/S = 3,5, FeO + MnO = 25 [2]

spinel formation [6, 7]. But the silica addition has the negative side effect that it reduces the castable strength at the ladle service temperature [8]. Previous papers [1, 2] introduced a novel binder based on calcium magnesium aluminate (CMA). The spinel crystals inside CMA are as small as generated in situ inside the matrix of an alumina magnesia castable. Improved slag resistance was found with CMA [2, 9] used in both alumina spinel and alumina magnesia castables (Fig. 1).

The micron-sized spinel phase homogeneously distributed in the CMA clinker and subsequently in the castable matrix via the CMA binder had been identified as the main reason for the improved penetration and corrosion resistance. Since the spinel inside CMA is of a similar size as reactive alumina it leads to the hypothesis that CMA not

only improves the penetration resistance but is also beneficial for the mechanical properties. The first part of this study highlights this aspect for alumina spinel castables with a range of different CMA contents. The second part focuses on CMA-based alumina magnesia castables and studies the effect of silica addition on castable properties. A specific focus is given to the role of silica in restraining or preventing hydration of the magnesia [10], which can lead to destructive cracks during dry out.

2 Test materials and test methods

The chemical and mineralogical composition of CAC and CMA are shown in Tab. 1. Both binders have a specific surface area of approx. 4000 cm²/g (*Blaine*) with a median grain size d_{50} of 15–18 μm. The chemical

Tab. 1 Composition of CAC and CMA [%]

Chemistry	Al ₂ O ₃	CaO	MgO	SiO ₂
CAC	68,7–70,5	28,5–30,5	<0,5	0,2–0,6
CMA	69–71	8–11	16–22	<1,0
Mineralogy	CA	CA2	MA	C2AS
CAC	63–67	33–37	0	<1
CMA	18–22	8–12	68–72	<1

Tab. 2 Chemistry of spinel and magnesia [%]

Chemistry	Al ₂ O ₃	CaO	MgO	SiO ₂	Fe ₂ O ₃
Fused spinel	74,1	0,4	24,7	0,3	0,2
Sintered spinel	77,0	0,2	22,5	0,1	0,2
Fused magnesia	0,4	1,4	95,3	1,9	0,9
Sintered magnesia	0,4	1,3	94,5	3,5	0,1

compositions of the sintered spinel (SSP), fused spinel (FSP), sintered magnesia (SM), and fused magnesia (FM) that were used are shown in Tab. 2.

Alumina spinel castables (Tab. 3) with different contents of CAC and of CMA and with different spinel types, namely sintered spinel, fused spinel, microspinel phase contained within CMA have been studied to analyse the sintering reactivity.

Alumina magnesia model castables (Tab. 4) with CAC and with CMA have been formulated to achieve equivalent total chemical compositions. The impact of silica fume on thermomechanical properties as well as dry-out has been investigated. Furthermore the influence of the magnesia type and content has been studied.

The amount of mixing water and the quantity of the deflocculant (polycarboxylate Peramin® AL 200) has been adjusted to achieve the same initial fluidity for all the mixes.

Placed properties: The prepared mix is placed by vibration into a 160 mm × 30 mm × 30 mm stainless mould and left for curing at 20 °C, 100 % rH for 24 h. Then, the parallelepipedic samples are removed from the mould and undergo a thermal treatment at 110 °C for 24 h, and at 1350 °C and 1600 °C for 6 h before the measurement of strength. Physical properties have been determined in accordance with EN 1402. Bulk density and apparent porosity of each specimen fired at different temperatures were also measured by the *Archimedes* method in water. PLC was also determined for all materials as a function of firing temperature and compared with dimensions obtained after curing at 110 °C.

Elastic properties: Measurements of the elastic modulus $E = f(T °C)$ of the specimens was made via a high temperature ultrasonic technique [11]. The value of *Young's* modulus of the material is obtained from the measurement of the time delay τ between two successive echoes through the sample. The characteristics of the different ultrasonic line have been adapted to the highly heterogeneous refractory castables with large grains and high porosity (up to 20 %), which involve a high ultrasonic attenuation: the dimensions of samples and the wave frequency are 100 mm × 10 mm × 10 mm and 35 kHz respectively. Due to this constraint of dimension for the specimens, all cast mater-

ials were sieved below 2 mm to remove the coarse aggregate. The paste was placed into the specific mould. Materials were cured at 20 °C/100 % rH for 24 h and after treated at 110 °C for 24 h again. Ultrasonic experiments have been performed during a thermal treatment consisting of a heating and cooling rate of 5 °C/min from room temperature to 1600 °C, with a dwelling time at 1600 °C for 1 h. The Young's modulus at 450 °C has been used as reference value (E_0).

Thermal shock: Tests were performed according to the EN-993-11 method. Four specimens 232 mm × 55 mm × 65 mm of each castable composition (depending upon silica content) were cast to measure the thermal shock damage. This test was conducted by quenching a sample 5 times into air with a pressure of 1 bar. Prior to quenching, each sample was fired at 1600 °C for 6 h and after cooling, reheated at 1200 °C for 1 h before each thermal shock.

Hydration resistance: The resistance of the magnesia in alumina magnesia castables to hydration has been simulated by hydrothermal treatment in an autoclave. In order to simulate the impact of in situ steam pressure during the dry-out of LCC's as a function of MgO quality and silica content, a hydrothermal treatment has been performed using a specially designed autoclave on parallelepipedic bars (the same as for strength measurement). MgO is more susceptible to transform into brucite under hydrothermal conditions [12]. For this test, after prepared bars were cured at 20 °C/100 % rH for 24 h, the materials were then treated for 6 h at 125 °C and 150 °C with a vapour pressure of 1,5 and 4 bar respectively. Mineralogical evaluations were also performed by XRD

Tab. 3 Alumina sintered spinel (SSP) and alumina fused spinel (FSP) model castables with CAC and with CMA [%]

	SSP/FSP 3-CAC	SSP/FSP 5-CAC	SSP/FSP 6-CAC
Tabular alumina 0–6 mm	67	67	60
Reactive alumina	10	8	11
Spinel, SSP or FSP <1 mm	6	6	13
Spinel, SSP or FSP <0,09 mm	14	14	10
SECAR® 71	3	5	6
Peramin® AL200	+0,1	+0,1	+0,1
Water	+3,9/4,0	+3,9/4,0	+3,9/4,0
Total MA	20,0	20,0	23,0
Total CaO	0,84	1,40	1,68
	SSP/FSP 6,5-CMA	SSP/FSP 9-CMA	SSP/FSP 13-CMA
Tabular alumina 0–6 mm	65,5	63	61
Reactive alumina	8	8	6
Spinel, SSP or FSP <1 mm	6	6	6
Spinel, SSP or FSP <0,09 mm	14	14	14
CMA 72	6,5	9	13
Peramin® AL200	+0,1	+0,1	+0,1
Water	+3,9/4,0	+3,9/4,0	+3,9/4,0
Total MA	24,7	26,5	29,4
Total CaO	0,62	0,86	1,24

quantitative analysis for materials treated at different autoclave temperatures (*Brucker* type D8 Advance) in order to measure the quantity of brucite resulting from the treatment.

3 Results and discussion

3.1 Alumina spinel castables

As can be seen in Fig. 2 strength after drying is very similar for CAC and CMA at equivalent

total CaO contents in the castable. But, when fired to 800 °C strength is about 20 to 50 % higher with CMA. This indicates a higher sintering reactivity when CMA is used in the castable matrix. Furthermore the fused spinel used in this study creates higher strength than the sintered spinel. This might be caused by the slightly smaller median particle size d_{50} of the fused spinel and/or the lower water demand compared to the sintered spinel.

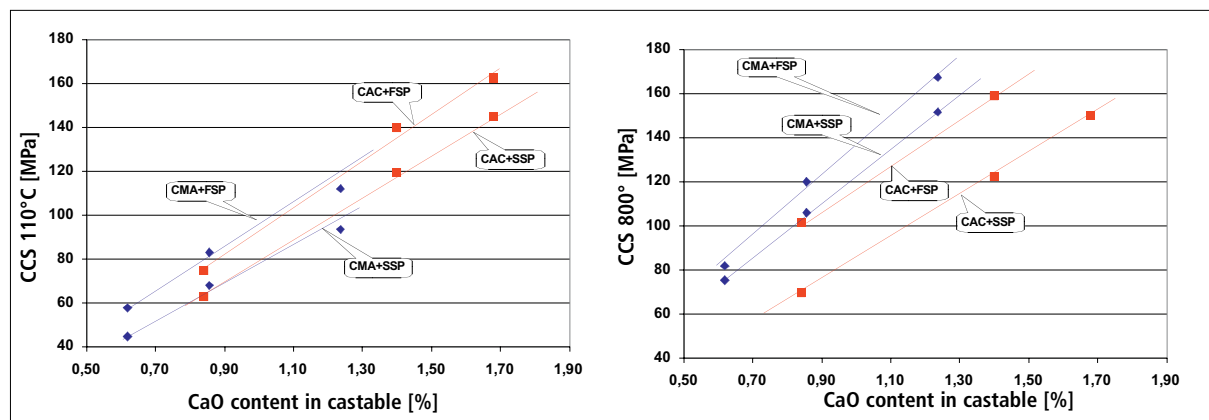


Fig. 2 Cold crushing strength (CCS) after drying at 110 °C and firing at 800 °C for CAC and CMA based alumina spinel castables (see Tab. 3)

Tab. 4 Alumina magnesia model castables (SM = sintered MgO, FM = fused MgO) with different amount of silica with CAC and CMA

	SM CAC	FM CAC	SM CMA	FM CMA
Tabular alumina 0–6 mm	71	71	65	65
Tabular alumina –325 mesh	5,5–4,5	5,5–4,5		
Tabular alumina <48 mesh			6–5	6–5
Reactive alumina	11	11	8	8
Sintered MgO –200 mesh	6,5		3	
Fused MgO <0,09 mm		6,5		3
Elkem Microsilica® 971U	0–1	0–1	0–1	0–1
SECAR® 71	6	6		
CMA 72			18	18
Peramin® AL200	+0,15	+0,15	+0,10	+0,10
Water	+4,5	+4,5	+4,5	+4,5
Total MA after firing	24	24	24	24
Total CaO	1,7	1,7	1,7	1,7

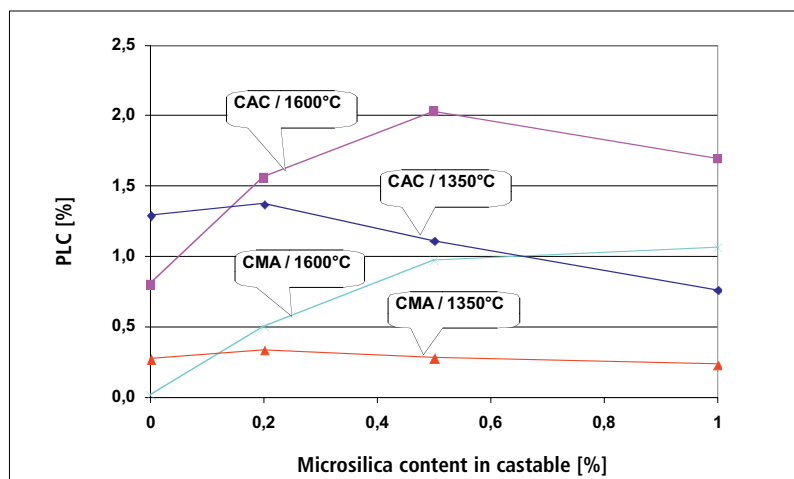


Fig. 3 Permanent linear change of castables SM-CAC and SM-CMA

The higher sintering reactivity of CMA is also indicated by the permanent linear change (PLC). CAC gives a slightly positive PLC with values between zero and 0,2 % and with the higher values achieved with the

higher CAC content. In case of CMA a small shrinkage of 0,1 to 0,2 % was observed with little impact by the quantity of CMA on PLC. With the fused spinel less shrinkage and more expansion was found than with

Tab. 5 Summary of the effects of silica content upon properties of alumina-magnesia castables

Silica Content [mass-%]	0–0,5	0,5–1
Sintering Reactivity		
Intergranular viscous phase	++	
Liquid phase	+	++++
PLS		
In situ spinel (>1000 °C)	1350 °C Poro →+++	1350 °C Poro ↗ +
CA ₆ -CMAS (>1350 °C)	1600 °C RC → +	1600 °C RC ↘++++

the sintered spinel, both, with CAC and with CMA.

3.2 Alumina magnesia castables

When using CMA in alumina magnesia castables the amount of added magnesia can be reduced while corrosion resistance increases [2]. The negative impact of magnesia on the rheology is reduced and a decrease of the amount of deflocculant by 1/3 could be achieved to keep the same initial fluidity. As less spinel needs to be formed in situ, the amount of non-reversible expansion was found to be smaller at constant amount of silica fume addition to the castable (1 %) [2].

The reduction of silica has a significant influence on the thermophysical properties. Even at reduced silica content the PLC remains small when CMA is used. The PLC after firing at 1350 °C increases as silica content reduces and reaches a maximum at 0,2 % silica fume (Fig. 3).

But the increase of PLC with reduction of silica is smaller with CMA since less periclase need to be added compared to CAC and hence less spinel need to be formed in situ. But it might be also the effect of a higher sintering reactivity of CMA since the PLC remains even quite low when no silica is added. When fired to 1600 °C the PLC is quite different. When silica is reduced from 1 % to 0,5 % the PLC first increases as expected for CAC but then drops again when silica fume is reduced below 0,5 %. In case of SM-CMA the PLC reduces when silica is reduced from 1 to 0,5 %. The PLC after firing at 1600 °C is generally higher with silica fume than without. This might be the consequence of the formation of less dense Ca-Mg-Al-Si-oxide phases when silica is present and/or of the degree of spinel formation and size of spinel crystals formed. In case of castable SM-CMA the volume stability is again higher than for SM-CAC. No significant difference was found when the sintered magnesia (SM) was replaced by the fused magnesia (FM). The PLC at intermediate temperatures between 1350 °C and 1600 °C need to be further investigated. Tab. 5 summarises the compromise between the effects obtained for the expansive formation of in situ spinel (1000–1400 °C) and those obtained for expansive formations of CA₆/CMAS phases with respect to the silica content.

The high temperature Young's modulus measurement of the castable matrix (<2 mm) indicates a visco-plastic effect (Fig. 4). With increasing silica content a more marked softening of the pure castable matrix occurs accompanied by a decrease in softening temperature. It is assumed that this visco-plastic behavior improves the capability to accommodate the linear expansion caused by the spinel formation inside a ladle wall. Two effects are observed with a decrease in the amount of silica: firstly, a strengthening of the microstructure from 800 to 1200 °C with CAS phase transformations and secondly, during the sintering process after 1200 °C which appears more enhanced in the case of reduced silica.

The results of thermal shock resistance using materials with 1 mass-% silica fume revealed a quasi-brittle behaviour resulting from the glassy phase previously formed at high temperature during the first heating-up. This was true for both the reference system as well as the CMA model formulation where rapid damage of the specimen was observed after the first thermal shock and then increased over the 5 cycles. Decreasing (Fig. 5) silica content down to 0,5 mass-% and 0,2 mass-% in the CMA model formulations rapidly and significantly increases the thermal shock resistance with less damage after each cycle relative to the system at 1 % silica.

With the reduction of the silica content the apparent porosity reduces from 19,7 % with 1 % silica to 15,1 % without silica after firing at 1600 °C of mix FM-CAC. SM-CAC gave generally a 2 %-points higher porosity than FM-CAC. With the CMA based castables porosity has been found 2–3 %-points lower than with the CAC based mixes.

The reduction of silica fume leads to a higher hydration degree of magnesia during drying, up to the point of cracking. This has been found on castable cubes of 10 mm × 10 mm × 10 cm after drying at 110 °C. Slightly more and bigger cracks have been found with the fused magnesia compared to the sintered magnesia. With CMA and 3 % magnesia the castable remain crack-free even at only 0,2 % silica fume.

These effects were further investigated using the previously described autoclave to simulate dry out behavior of blocks or sections where hydrothermal conditions may occur inside the block. Since CMA based samples

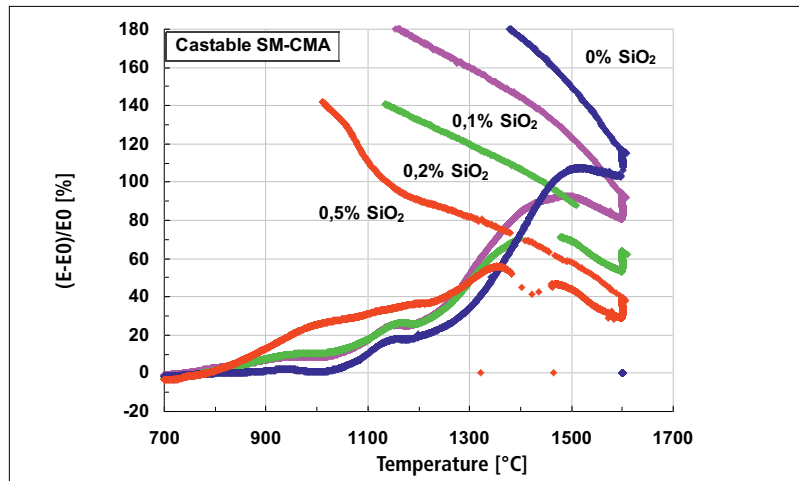


Fig. 4 Young's modulus evolution during first heat-up to 1600 °C (samples pre-dried at 110 °C)

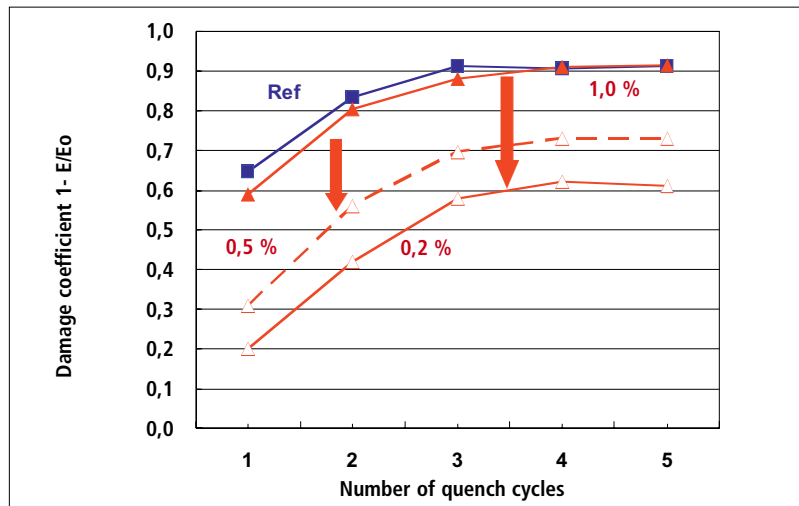


Fig. 5 Evolution of the damage (calculated from E-modulus) of CMA castable with number of thermal shocks

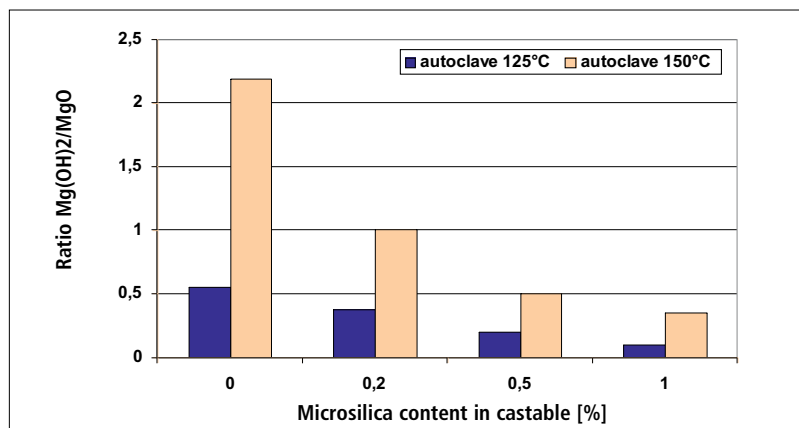


Fig. 6 Magnesia hydration rate in castable FM-CMA as function of silica content and autoclave temperature

contain less magnesia than CAC samples, the MgO hydration resistance after autoclave treatment is estimated by XRD meas-

urement with a ratio between brucite and non-hydrated MgO. Hydrothermally treated castable prisms (3 cm × 3 cm × 8 cm)

showed that with increasing silica content the ratio between formed magnesium hydroxide (brucite) and unreacted magnesium oxide (periclase) reduces (Fig. 6). The MgO hydration under hydrothermal conditions is much larger at 150 °C than at 125 °C. But when silica is reduced from 1 to 0,3 % no cracks occurred with CMA. Contrary to that the sample with CAC was heavily cracked when silica was reduced to 0,3 %. However, when further reduced to 0,2 % even the CMA based castable started to crack.

It was also found that the hydration of fused MgO seems to be more sensitive than sintered MgO, in particular with low silica content where brucite can be rapidly formed even at 125 °C. The ratio of peak heights for the sintered magnesia reached a maximum of 1,6 at 150 °C compared to 2,2 measured with the fused magnesia (Fig. 6) at zero silica content. As discussed above, the treatment at 150 °C is more aggressive with respect to brucite formation than 125 °C and the hydration of sintered magnesia follows this logic but rapidly decreases with increasing silica content. Above 0,5 % silica almost no brucite can be detected after treatment at 125 °C or 150 °C.

These effects can be summarised as follows. The advantage of CMA is that the magnesia content can be reduced, relative to reference systems, which improves hot properties. At the same time this reduced silica addition is sufficient to eliminate any negative effects arising from magnesia hydration on dry out. The final level of silica chosen can therefore be selected on the basis of target thermal mechanical properties (high temperature

rigidity vs. plastic behavior) rather than an amount necessary to block the magnesia hydration.

4 Conclusions

CMA, the new calcium magnesium aluminate contains microspinel homogeneously distributed between calcium aluminate phases. It brings improved corrosion resistance but also supplementary sintering reactivity and strength to ladle castables. With CMA, low apparent porosity can be achieved in alumina magnesia castables. CMA allows a reduction in the added magnesia content and then it is possible to reduce the silica fume content. This improves the volume stability during the first heat-up and increases the hot strength. The thermal shock resistance is improved when the ladle has to be cooled down to room temperature. However it is recommended that a small amount of silica be kept inside alumina magnesia castables as it reduces magnesia hydration and prevents crack formation during drying.

Acknowledgment

The authors would like to thank the *Kerneos Laboratories* in France and China for the support of this study.

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