

The Hydration Behaviour of MgO–SiO₂–H₂O Gel Bonded MgO Castables

H. Peng, B. Myhre

Although high-performance refractory castables play an essential role in state-of-the-art steel-making, magnesia castables have not been widely used yet. One of the major challenges is brucite formation during MgO hydration, which causes volume expansion and subsequent cracking – a phenomenon commonly called “slaking”. To overcome these problems, a new specialty product (SioxX-Mag) has recently been developed for cement-free MgO castables based on the MgO–SiO₂–H₂O bond. In this paper, systematic work has been carried out in order to understand the MgO hydration and to make crack-free MgO castables. Using SioxX-Mag in conjunction with microsilica, the cracking caused by the brucite formation is suppressed and crack-free dried large blocks can be made. Samples taken from the inner parts of the large blocks were investigated by XRD techniques after hydration during drying-out process. The results demonstrate that microsilica is an effective anti-hydration additive for MgO castables. When 8 % microsilica was used, MgO hydration was inhibited and no brucite phase was detected and crack-free large MgO castable blocks were made. With less microsilica (e.g. 6 %), brucite forms during drying-out process and cracks are observed in the blocks.

1 Introduction

It is well-known that magnesia castables are not widely used, mainly due to brucite formation (Mg(OH)₂). The brucite formation causes volume expansion and subsequent cracking, a phenomenon commonly called “slaking” [1–3]. Earlier research has demonstrated that the interaction between MgO and SiO₂ prevents slaking [4–6]. Already in 1989, Elkem started work on a new binder system for basic castables based on the reaction between MgO fines, microsilica (SiO₂) and water. An important observation was that no slaking occurred at 6 % microsilica addition.

The hydration of magnesia and dehydration of brucite have been thoroughly studied during the last decade [7–12]. The parameters affecting the hydration of MgO castables can be summarized as follows:

- particle size, reactivity and ratio of CaO/SiO₂ in MgO raw materials, especially MgO fines;
- additives, such as dispersants/water-reducing agents, retarders and/or accelerators, contribute to slow down and/or to control the speed of the chemical reaction

between MgO and water, i.e. minimizing the brucite formation;

- microsilica fines;
- dry-out profile; and
- water addition.

Various technologies have been reported to inhibit and/or ultimately avoid the brucite formation by including microsilica as anti-hydration agent, fibres as drying agent to accelerate water evaporation, and optimization of additives and water addition to minimize water available for brucite formation after placing.

At ALAFAR 2012, Peng et al. [13] presented preliminary results using a new product, “SioxX-Mag prototype”, designed to promote the bond system MgO–SiO₂–H₂O for cement-free MgO castables. Since then, the effect of additives and/or microsilica on slaking, flow and the setting mechanism has been further investigated. It has been demonstrated that microsilica addition has a strong influence on flow, setting and slaking of cement-free MgO castables [14]. It was reported that 3 % microsilica effectively suppressed cracking, while at lower dosage cracking was easily recognizable. With sub-micron alumina alone cracking was very pro-

nounced. This indicates that microsilica is an efficient anti-hydration agent, while alumina does not give protection against slaking. It is also noticed that the studies on hydration of MgO described above are mostly based on “MgO containing” castables, such as spinel-magnesia castables with cement [7–12]. Little work has been done on MgO-rich cement-free castables. Moreover, most of the results mentioned above are based on labo-

Hong Peng, Bjørn Myhre
Elkem Silicon Materials
Kristiansand
Norway

Corresponding author: *Hong Peng*
E-mail: hong.peng@elkem.no

Keywords: MgO castable, brucite formation, crack-free, gel-bonded, microsilica

Received: 25.11.2014

Accepted: 02.02.2015

The paper was awarded with the 1st prize at ALAFAR 2014

Tab. 1 Composition of microsilica-gel bonded MgO castables

[mass-%]		MgO-REF	Mag-A	Mag-B	Mag-C	Mag-D
Synthetic DBM 99	5–3 mm	12	12	10	10	10
	3–1 mm	24	24	35	35	35
	1–0 mm	27	27	20	20	20
	100 mesh	10	10	6	6	6
	325 mesh	21	21	20	20	20
Microsilica	Elkem 971U	6	6	8	6	6
Alumina	Sub-micron				3,2	3,2
PP fibre						0,1
Dispersants		Disp. A	SioxX-Mag			

ratory results, and few studies on real-size MgO castables have been reported [2]. Dry-out of large objects is challenging in comparison to small lab-scale samples. During the dry-out stage the MgO hydration of the inner part of larger samples may be accelerated due to higher vapour pressure and prolonged contact time with water in comparison to the outer part.

This paper is focused on the hydration of MgO in pure MgO castables using MgO–SiO₂–H₂O as binder system. The objectives are:

- to understand the effect of dispersants and microsilica on hydration of MgO in large samples,
- to introduce a speciality product, SioxX-Mag, purposely designed for magnesia castables to overcome the problem related to slaking and to develop crack-free MgO castables, and
- ultimately to develop MgO castables with high performance. The results demonstrate that sufficient microsilica in combination with optimum dispersants are the key factors in obtaining crack-free large

magnesia castable samples. High-performance basic refractory castables with 8 mass-% high quality microsilica in conjunction with SioxX-Mag were developed.

2 Experimental

2.1 Composition design

The overall particle size distributions (PSD) for the compositions were calculated using the EMMA program [15]. EMMA is free software based on the Andreasen model and is widely used for evaluation and optimization of particle packing in refractory castable mix design. In the present study, the q-value of sample MgO-REF and Mag-A is 0,25, while the others have a q-value of 0,24. Tab. 1 presents the compositions of the magnesia castables using MgO–SiO₂–H₂O as binder system. Synthetic dead-burned MgO (Nedmag 99, labelled Synthetic DBM 99) with different particle fractions and high quality microsilica (Elkem 971U) were used as raw materials. The dispersant was SioxX-Mag. For comparison, a castable containing 6 mass-% microsilica and a different addi-

tive, denominated Disp. A, was made. The dosage level of each dispersant was optimized. Based on Mag-B, extra sample Mag-C was designed, where 2 mass-% microsilica was replaced by the same vol-% submicron alumina, i.e. 3,2 mass-% alumina. Water addition was kept at approximately 5,5 % for all mixes.

2.2 Properties measurement and characterization

Self-flow and vibration-flow of the fresh mix were measured using the flow-cone described in ASTM C230 (height of 50 mm, not the more recent cone of 80 mm described in EN 1402-4:2003). The self-flow value is the increase in percent of the diameter of the fresh mix measured 90 s after removing the cone. The material was then cast into 25 mm × 25 mm × 150 mm moulds for Hot Modulus of Rupture (HMOR) measurement. The moulds were kept at 20 °C and RH >90 % for 24 h before de-moulding, then dried at 110 °C for 24 h. All lab-scale small prisms were crack-free.

The castables were also cast into larger moulds with dimensions:

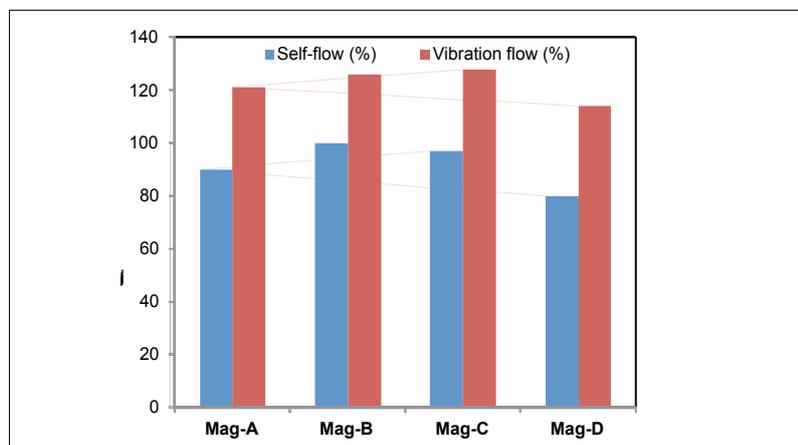
- 300 mm × 300 mm × 300 mm (~75 kg) and
 - 300 mm × 300 mm × 150 mm (~37,5 kg).
- They were de-moulded after one day and air-cured at ambient temperature for another two days before the dry-out started. The following dry-out profile was used [2]:
- 5 °C/min from room temperature to 80 °C,
 - 5 h at 80 °C,
 - 5 °C/min from 80 to 150 °C, and
 - 12 h at 150 °C.

Afterwards, the furnace was turned off and left to cool. The dried large samples were photographed and samples from the core were taken for characterization. An X-ray diffractometer (XRD, X'Pert Pro, Philips/NL) with CuK α radiation was used for the mineralogical phase analysis. A Scanning Electronic Microscope (SEM, Quanta 400, FEI Company/US) was used for examination of the microstructure on polished surfaces of the samples.

3 Results and discussion

3.1 Flowability and set behaviour of MgO castables

The flowability of MgO–SiO₂–H₂O bond magnesia castables has been evaluated. The

**Fig. 1** Self-flow (SF) and vibration-flow (VF) of magnesia castables

self- and vibration-flow at 5,5 mass-% water addition are summarized in Fig. 1. Self-flow around 100 % and vibration-flow of 120–130 % are achieved for the samples Mag-A, -B and -C. With addition of 0,1 % PP fibres, mix called Mag-D, the self-flow value drops slightly but is still sufficient, ~80 %. It is demonstrated that self-flowing MgO castables can be made with SiOX-Mag and high quality microsilica.

As gel-bonded MgO castables do not give good temperature readings using exotherm curves, the propagation of ultrasound was used to monitor the setting and hardening process. Fig. 2 shows the ultrasonic velocity development for magnesia castables. As stiffness and speed of sound are closely related the increase of velocity indicates end of working time and initial set. The results demonstrate that the setting and hardening process are similar when the microsilica content increases from 6 to 8 mass-%. The working time of castables with SiOX-Mag as dispersant is approximately 1,5 h. It is also interesting to notice that the setting is fast after initial set.

3.2 Hydration behaviour of MgO

It has been reported that crack-free lab-scale samples were made at microsilica dosage above 3 % and that MgO castables containing 6 % microsilica without alumina outperformed others in terms of hot properties [14]. In this work we use MgO castables with 6 % microsilica as benchmark (MgO-REF and Mag-A, see Tab. 1), other samples with both higher microsilica content and addition of submicron alumina were included in order to investigate the MgO hydration behaviour and possible cracking of large blocks. All lab-scale small prisms discussed in this paper were crack-free.

Blocks (300 mm × 300 mm × 150 mm) of MgO-REF and Mag-A, -B and -C were firstly made. When de-moulded after 1 day, all blocks were perfect, no cracks were observed. After curing one more day in air, all blocks were dried at 150 °C for 12 h. Fig. 3 shows the MgO blocks after dry-out. Cracks were observed in the block MgO-REF, going through the whole body; whereas blocks Mag-A, -B and -C are perfect.

When the MgO-REF is compared to Mag-A, the only difference is the type of dispersant. MgO-REF contains Disp. A and Mag-A is made with SiOX-Mag. Seemingly, the dis-

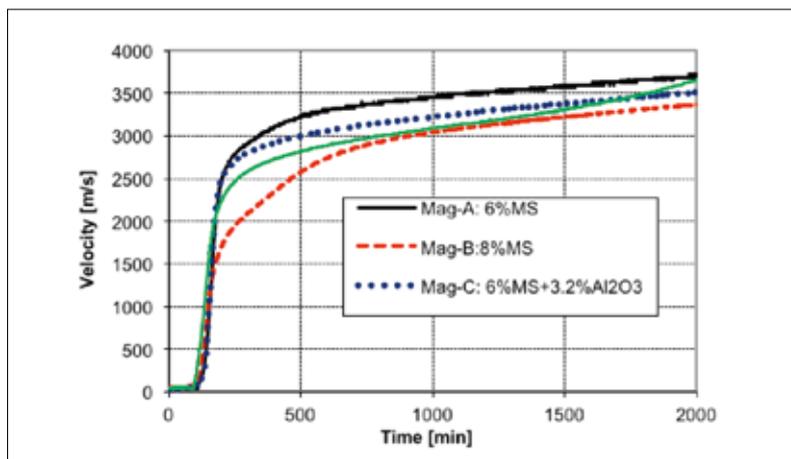


Fig. 2 Setting and hardening process of magnesia castables

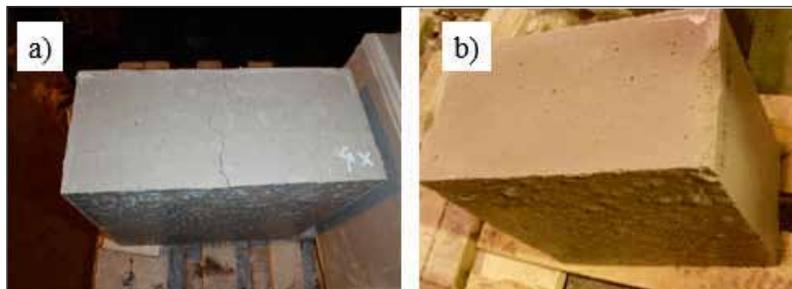


Fig. 3 a–b Blocks (300 mm × 300 mm × 150 mm) after dry-out a) MgO-REF and b) Mag-A; Mag-B and -C looked similar to Mag-A

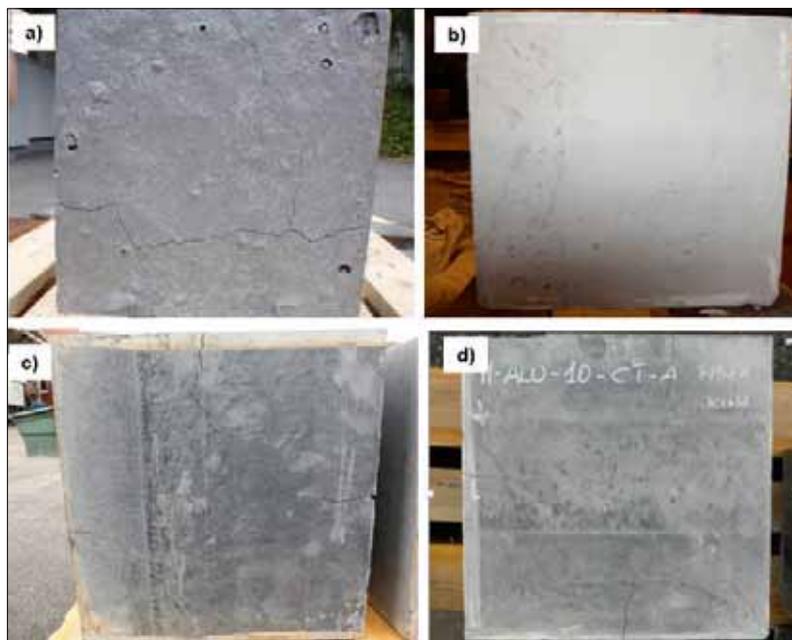


Fig. 4 a–d Blocks (300 mm × 300 mm × 300 mm) after dry-out at 150 °C for 12 h: a) Mag-A with 6 % microsilica, b) Mag-B with 8 % microsilica, c) Mag-C with 6 % microsilica + 3,2 % alumina, and d) 6 % microsilica + 3,2 % alumina + 0,1 % PP fibres

persants and sizes of the samples have significant impact on crack formation during dry-out.

Blocks with doubled thickness (300 mm) of Mag-A, -B, -C and -D were made in order to check how the thickness and microsilica

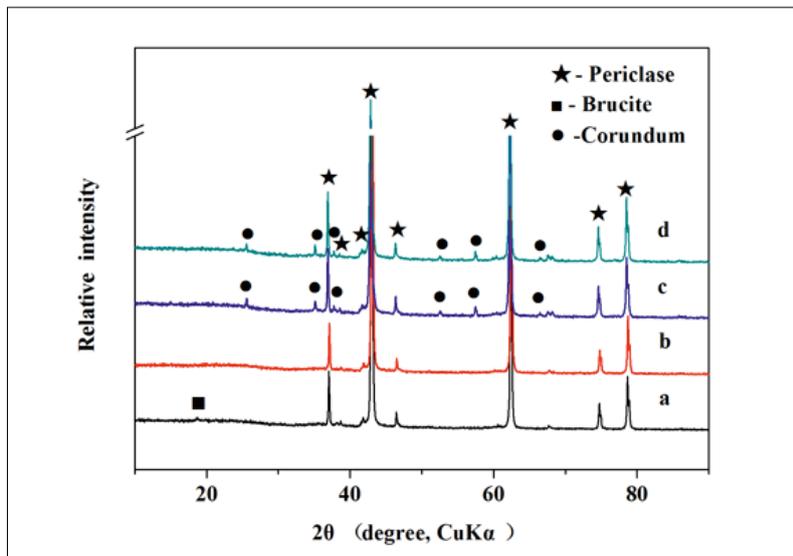


Fig. 5 XRD patterns after dry-out at 150 °C for 10 h: a) MgO-A with 6 % microsilica, b) Mag-B with 8 % microsilica, c) Mag-C with 6 % microsilica + 3,2 % alumina, and d) Mag-D with 6 % microsilica + 3,2 % alumina + 0,1 mass-% PP fibres

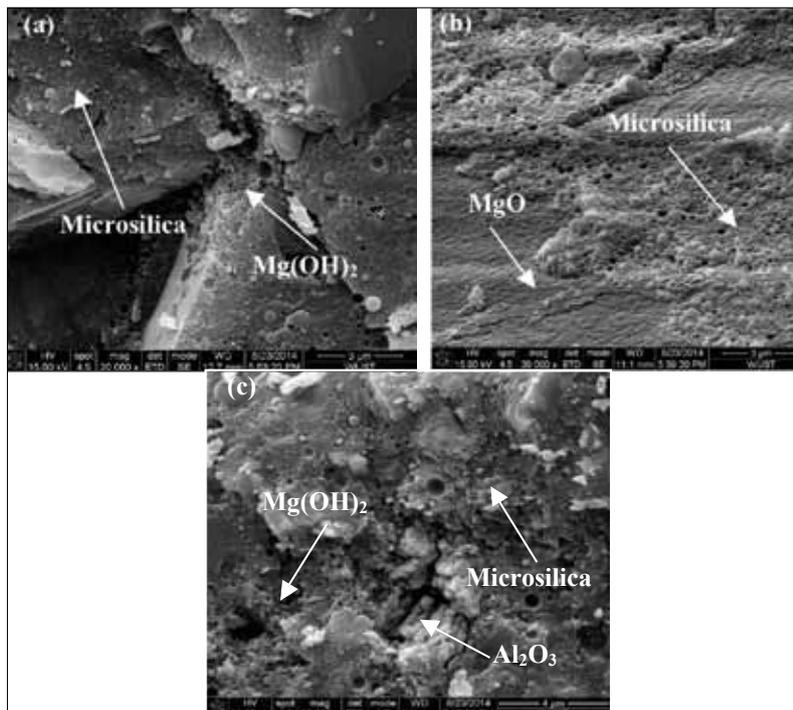


Fig. 6 a–c SEM micrographs of fractured surfaces of MgO blocks after dry-out at 150 °C for 12 h: a) MgO-A with 6 % microsilica, b) Mag-B with 8 % microsilica, and c) Mag-C with 6 % microsilica + 3,2 % alumina

content affect the hydration and subsequent cracking, as shown in Fig. 4. Mag-B with 8 % microsilica did not crack, while Mag-A with 6 % microsilica and Mag-C and -D with 6 % microsilica in combination with 3,2 % submicron alumina had small cracks. Based on Mag-C, an extra block with addition of 0,1 % PP fibres was made. In this case, the

addition of fibres did not prevent crack formation. As illustrated in Fig. 3 and 4, the type of dispersants, the amount of microsilica, the addition of submicron alumina, and the thickness of the samples seem to have strong impact on the hydration of MgO and subsequent cracking of the dried larger blocks.

In order to understand the MgO hydration mechanism samples from the larger blocks were used for a mineralogical phase analysis using XRD and SEM characterisation. Fig. 5 presents the XRD patterns. The Mag-A with 6 mass-% microsilica contains mainly periclase (MgO) and small amounts of brucite. In Mag-B with 8 mass-% microsilica, only periclase is observed and no brucite phases could be detected. The major difference in composition of Mag-A and Mag-B is the microsilica content; 6 % and 8 % respectively. In Mag-C and -D, periclase and corundum (alumina) were observed. Furthermore, no magnesia silicate hydrate (M-S-H) could be detected in any of the four samples, indicating that the M-S-H has poor crystallinity. Fig. 6 shows the SEM microstructure of the fractured surfaces. In Fig. 6 a) and c), the $Mg(OH)_2$ crystals can be observed as fibrous rosettes exhibiting its trigonal crystal system (hexagonal scalenohedral). The addition of submicron alumina does not provide protect against brucite formation. In this case, 6 % microsilica seems to be sufficient to fill all the gaps/pores to obtain close packing and good flowability. However, it is not enough to cover all the surfaces of the MgO. Some MgO fines in the matrix will be exposed to water during placing and will hydrate to some extent, and brucite will form. When 8 % microsilica is used (Fig. 6 b), all the surfaces of the MgO are covered and MgO hydration is prevented, hence no brucite is seen.

As demonstrated in both Fig. 5 and Fig. 6 a higher dosage of microsilica seems to be an effective way to prevent and/or slow-down brucite formation during the curing and drying process. When 6 % microsilica is used, the MgO hydration is obviously reduced to a great extent, and this results in crack-free lab-scale prisms as well as blocks with dimension of 300 mm × 300 mm × 150 mm as the water evaporates relatively fast. However, when larger blocks such as those with double thickness (300 mm) are made, cracking may occur during the dry-out process. In larger blocks, the contact time with water at the core is longer than in small samples and the hydration of MgO at the centre is accelerated due to high vapour pressure and availability of water locally. By using SiOX-Mag and 6 % microsilica, crack-free blocks with a thickness of 150 mm have been made. If more thickness

is needed, adding more microsilica seems to be an alternative. The mechanisms of how dispersants, drying agent and drying profile affect the MgO hydration in large samples are not fully understood yet. Further investigations are ongoing and will be reported in the future.

3.3 Hot Modulus of Rupture (HMOR) and Refractoriness Under Loading (RUL)

HMOR is plotted as a function of test temperatures in Fig. 7. For Mag-A, -B and -C, the development of H.M.O.R. is similar, reaching a maximum value at 1300 °C. When 2 mass-% microsilica in Mag-B is replaced by same volume of micro-alumina (3,2 mass-% alumina in Mag-C), the H.M.O.R. is reduced at test temperatures above 1300 °C. For example, at 1400 °C, the HMOR of Mag-C containing 8 mass-% microsilica is ~8 MPa, being ~30 % higher than that of Mag-C.

In order to better understand how the bond phases contribute to the hot properties of the MgO castables, the phase compositions of Mag-A, -B, -C after H.M.O.R. test at 1500 °C were analysed using XRD. Fig. 8 shows the XRD patterns. Both Mag-A and -B contain mainly periclase (MgO) and forsterite. In Mag-C, when 2 mass-% microsilica is replaced by sub-micron alumina, spinel is observed in addition to periclase and forsterite. This shows that microsilica and sub-micron alumina react with MgO fines at high temperatures, and are transformed to forsterite and spinel respectively. Forsterite contributes to better hot-properties, while the presence of spinel seems to result in lower hot-strength (Fig. 6).

4 Conclusions

The study on crack formation, XRD and SEM characterization of samples from larger blocks after dry-out, as well as work on hot properties of self-flowing MgO castables, provide valuable information in the work to understand the MgO hydration and to further develop MgO castables with high performance.

- The mechanism of hydration of MgO in larger MgO castable blocks seems to be different from that in lab-scale specimens. In larger blocks, both microsilica dosage and the type of dispersant affect MgO hydration and related cracking during the

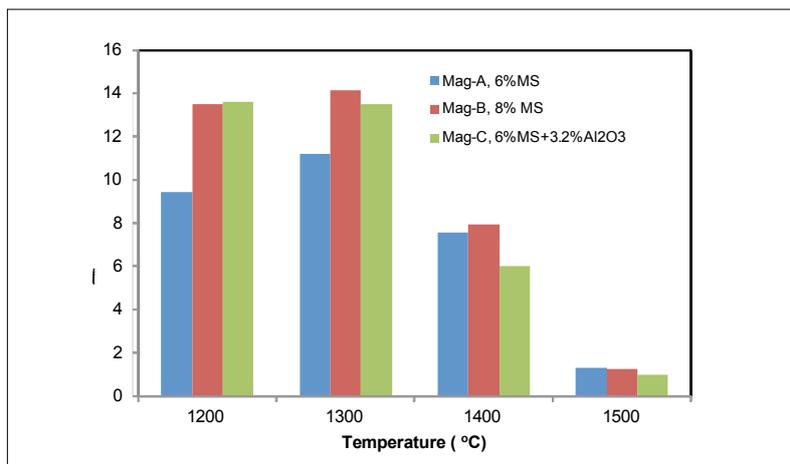


Fig. 7 HMOR as a function of test temperature

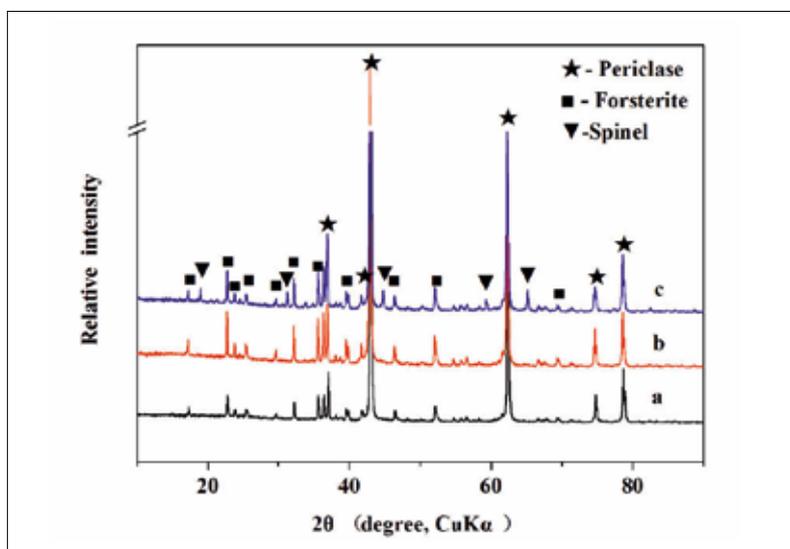


Fig. 8 XRD patterns of MgO castables after HMOR test at 1500 °C: a) Mag-A with 6 % microsilica, b) Mag-B with 8 % microsilica, and c) Mag-C with 6 % microsilica + 3,2 % submicron alumina

dry-out process. Microsilica in combination with SiOX-Mag seems to be an efficient "anti-hydration solution".

- XRD characterization confirms that brucite formation can be avoided, provided sufficient microsilica is present. Only trace amounts of brucite were detected at 6 % microsilica, whereas no brucite was found at 8 %. Crack-free larger blocks, 300 mm × 300 mm × 300 mm (~75 kg), were produced. It is also confirmed that microsilica reacts with MgO fines and transforms to forsterite at high temperatures.
- MgO castables with high quality microsilica and SiOX-Mag have been developed, exhibiting good placing properties and high hot-strength. The bond system MgO–

SiO₂–H₂O contains only small amounts of bound water. Once the free water is removed, the castables can be fired at very high heating rates.

Acknowledgements

The authors wish to thank Liao Ning from Wuhan University of Science and Technology (FIRE student) for XRD and SEM characterization.

References

- [1] Watanabe, Y.; et al.: Development and application of Monolithic Refractory Containing Magnesia Clinker. Proc. 2nd Int. Conf. Refractories. Tokyo, Japan (1987) 494–506
- [2] Silva, W.M.; Aneziris, C.G.; Modestino, A.M.B.: Effect of alumina and silica on the hydration

- behavior of magnesia-based refractory castables. *J. Amer. Ceram. Soc.* **94** (2011) [12] 4218–4225
- [3] Souzaa, T.M.; et al.: Phosphate chemical binder as an anti-hydration additive for Al_2O_3 -MgO refractory castables. *Ceramics Int.* **40** (2014) 1503–1512
- [4] Sandberg, B.; Mosberg, T.: Use of microsilica in binder systems for ultra-low cement castables and basic, "cement-free" castables. *Advances in Refractories Technology* **4** (1989) 245–258
- [5] Myhre, B.: Cement-free castables in the system MgO-SiO₂: The effect of bond phase modifiers on strength. Presented at 93rd Annual Meeting, Amer. Ceram. Soc. (1991)
- [6] Odegard, C.; Feldborg, H.; Myhre, B.: Magnesia-silica-hydrate bonded MgO castables". Proc. UNITECR'01, Mexico, 4–8th Nov. 2001
- [7] Ghanbari Ahari, K.; Sharp, J.H.; Lee, W.E: Hydration of refractory oxides in castable bond systems – II: alumina-silica and magnesia-silica mixtures. *J. Europ. Ceram. Soc.* **23** (2003) [16] 3071–3077
- [8] Salomão, R.; Pandolfelli, V.C.: Microsilica addition as an antihydration technique for magnesia-containing refractory castables. *Amer. Ceram. Soc. Bull.* **86** (2007) [6] 9301–9306
- [9] Salomão, R.; Bittencourt, L.R.M.; Pandolfelli, V.C.: A novel approach for magnesia hydration assessment in refractory castables. *Ceram. Int.* **33** (2007) [5] 803–810
- [10] Durán, T.; et al.: Interactions in calcium aluminate cement (CAC)-based castables containing magnesia. Part I: Hydration-dehydration behavior of MgO in the absence of CAC. *J. Amer. Ceram. Soc.* **94** (2011) [3] 902–908
- [11] Souza, T.M.; et al.: Systemic analysis of MgO hydration effects on alumina-magnesia refractory castables. *Ceram. Int.* **38** (2012) [5] 3969–3976
- [12] Sako, E.Y.; Braulio, M.A.L.; Pandolfelli, V.C.: Microstructural evolution of magnesia-based castables containing microsilica. *Ceram. Int.* **38** (2012) [7] 6027–6033
- [13] Peng, H.; Myhre, B.; Luo, M.: New additive packages for self-flowing high-alumina and MgO based refractory castables. Proc. ALAFAR 2012, Cancùn, Mexico, 5–8 Nov. 2012
- [14] Myhre, B.; Peng, H.; Luo, M.: Cement free MgO castables Part I, flow, setting and slaking. Proc. UNITCER'13, Canada 2013
- [15] EMMA (Elkem Materials – Mixture Analyzer) software, free download at: <http://www.materials.elkem.com/>