New Additive Packages for Self-flowing High-alumina and MgO Based Refractory Castables*

Hong Peng, Ming Luo, Bjørn Myhre

Self-flowing refractory castables with special performance are continuously being developed. New and improved dispersant systems play an essential role in this development. The objective of this paper is to highlight the benefits of two novel admixture systems that have been tested in various refractory castables.

SioxX/SioxX-Quick is a specialty additive package developed for use in microsilica containing alumina based castable systems. The main function of SioxX is to control flow properties whereas SioxX-Quick controls setting characteristics. In combination they will enable the castable producer to control flow and set time accurately. When SioxX replaces sodium hexametaphosphate, self-flow is improved by 20 to 30 % and shelf-life of dry premixes is significantly improved.

SioxX-Mag is a new additive package being developed for basic refractory castables. It contributes to better workability and setting behavior of MgO based castables while hot-properties remain unchanged. High performance, cement-free MgO castables based on MgO-SiO_2-H_2O bond using SioxX-Mag as dispersant have been tested. Using SioxX-Mag together with microsilica, slaking caused by brucite formation is suppressed and crack-free dried samples are made. Another benefit of using this additive package is the improved drying characteristics allowing fast firing of the castable.

1 Introduction

Characteristics of advanced self-flowing refractory castables are ease of installation, possibility to cast intricate shapes, energy savings and better performance in general. Important factors to control in these castables include particle size distribution (PSD), additives (deflocculants, dispersants, accelerators) [1, 2] and the raw materials, particularly with respect to the super-fines and cement [3, 4]. Numerous recent research programs have focused on understanding the mechanism of dispersion and optimization of dispersants for specific castables [5–8]. No doubt, dispersants continue to play an essential role in further development of advanced refractories.

For state-of-the-art steel-making and clean steel production high-performance basic refractory castables are of particular importance. Already in 1989, *Elkem Materials* started development work on a new binder system for basic castables based on the reaction between MgO fines, microsilica (SiO_2) and water [9]. This bond system was first applied to magnesia, silicon nitride and magnesia-carbon castables and required low water addition (5,0–5,5 %) resulting in adequate mechanical properties. An important observation was that at 6 % microsilica addition no slaking occurred. Since then, significant research on the use of microsilica in basic castables has been run [10–13], self-flowing cement-free MgO-SiO_2 bonded castables can be produced. About 6 mass-% microsilica seems to be essential to obtain both good placement and hot properties. A surprising observation is that the slag resistance to both BOF and EAF slag compared to an alumina spinel castable is improved [11]. Recently, many research programs have focused on hydration mechanism of magnesia with water and additives (dispersants and retarders) in systems such as MgO-SiO_2-H_2O, MgO-Al_2O_3-H_2O and MgO-SiO_2-Al_2O_3-H_2O [14–17]. However, self-flowing magnesia castables have not been widely used until

Hong Peng, Bjørn Myhre
Elkem Silicon Materials
4675 Kristiansand
Norway

Ming Luo
Wuhan University of Science and Technology
430081 Wuhan
China

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

Keywords: self-flowing, new dispersants, high-alumina and basic refractory castables, microsilica gel-bonding
Received: 21.11.2012
Accepted: 21.12.2012

* The paper was presented at ALAFAR in Cancún/MX in Nov. 2012 and received the 3rd prize of the ALAFAR Award 2012

Tab. 1 Composition of SiC based LCC [mass-%]

	Ref-I	SX-I	SX/SX-Q-I
Elkem Microsilica 971U	10	8,7	8
Cement	6	6	6
SiC	72	72	72
Calcined alumina	13	12,3	12
SHMP	0,2		
SioxX		2	2
SioxX-Quick			1
Water	5,50	5,50	5,50

now. One of the challenges is that during the hydration process brucite is formed which causes volume expansion and subsequent cracking – a phenomenon commonly called "slaking" [18]. Although it has been demonstrated that the interaction between MgO and SiO_2 prevents slaking, the mechanism has not been fully understood.

For more than 30 years, Elkem's focus has been on understanding the influence of microsilica on the properties of refractory castables. Microsilica (SiO_2) consists of spherical particles of amorphous silicon dioxide (SiO_2) with an average particle size of 0,15 µm (150 nm). The most important benefits of microsilica in castables are:

- Increased packing density
- Improved flowability, i.e. reduction in mixing water needed for a given flow [19]
- Contribution to high-temperature strength due to formation of mullite at temperature above 1300 °C in alumina based castables [20]
- Bond formation by interaction with MgO fines and avoidance of "slaking" during set and drying of MgO-based castables [14–17].

Based on our experience from the use of microsilica in different refractory castables, two types of additive packages have recently been developed. SioxX/SioxX-Quick is for high-alumina castables and SioxX-Mag for basic castables. For ease of application and improved functionality, high-grade microsilica is used as carrier in these products. As seen in the following this is compensated for in the mix design by reducing the microsilica dosage correspondingly.

2. Experimental

2.1 Composition design – SioxX/SioxX-Quick

SioxX/SioxX-Quick has been tested in a variety of refractory castables such as white fused, mulcoa and bauxite based systems [21]. Here, a SiC based LCC is selected to investigate the key parameters affecting shelf-life of LCC premixes and the impact of dispersants on the properties of self-flowing LCC. As seen in Tab. 1, 6 % cement was used. The Ref-I mix with sodium hexametaphosphate (SHMP) as dispersant is a type of mix used industrially and is the reference for comparison with SioxX/SioxX-Quick mixes.

To investigate the effect of humidity on shelf-life, dry-mixed 25 kg samples packed in closed, plastic lined paper bags were stored in a temperature and humidity controlled room ("climate room" with 70–80 % relative humidity at 20 °C). These storage conditions have been used several times before and give an accelerated ageing of the castable.

2.2 Composition design – SioxX-Mag

Concerning SioxX-Mag (prototype), cement free MgO-based castable is used to compare the effects of various dispersants on flow, MgO hydration mechanism and hot properties. Tab. 2 shows the composition of the castables with an optimized particle size distribution. Commercially available dispersants A and B and the new SioxX-Mag (prototype) from Elkem are used. The dosage level of the dispersants are optimized, 0,25 % for A and B, and 2 % for SioxX-Mag. The water addition is kept at 5,5 % for all mixes.

2.3 Measurements

Self-flow of the freshly mixed castable (after four minutes wet-mixing) was 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 of the diameter of the fresh mix measured 90 s after removing the cone.

Set time is normally defined as the time from mixing to the first noticed temperature increase in the mix. This is often referred to as the working time. Fresh samples were placed in insulated boxes and the time to onset of temperature increase recorded.

Cold modulus of rupture (CMOR) and hot modulus of rupture (HMOR) were measured. The HMOR testing apparatus (Isoheat, GB) is equipped with a pre-heating chamber such that 10 samples can be kept at the test temperature. The dried samples (25 mm × 25 mm × 150 mm) were heated at a rate of 300 °C/h.

Explosion resistance of the cement-free MgO-based castables was tested according to the Chinese Standard YB/T4117-2003. 50 mm cubes were placed into a furnace heated to a preset temperature. The cubes were inspected after 30 min exposure. The

Tab. 2 Composition of gel-bonded MgO based castable [mass-%]

		M1	M2	M3
Nedmag MgO	5–3 mm	12	12	12
	3–1 mm	24	24	24
	1–0 mm	27	27	27
	100 mesh	10	10	10
	325 mesh	21	21	20,5
Elkem Microsilica	971U	6	6	4,5
Dispersants	A	0,25		
	B		0,25	
	SioxX-Mag (prototype)			2
Water		5,5		

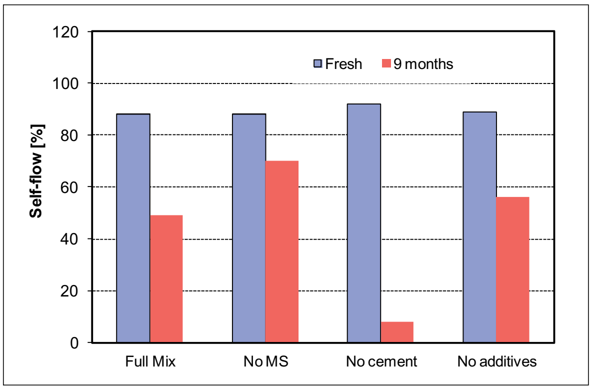

Fig. 1 Effect of 9 months storage on self-flow as a function of "missing" ingredient

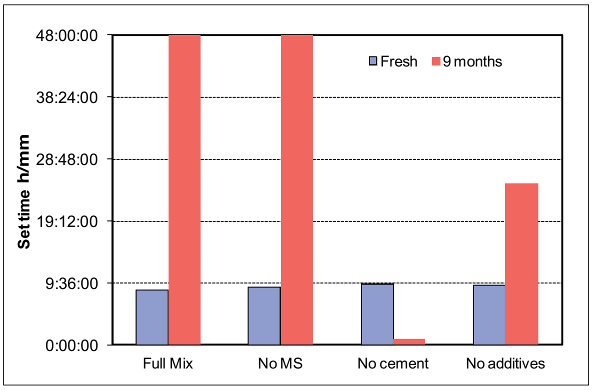

Fig. 2 Set-time after 9 months storage as a function of "missing" ingredient

temperature at which cracks start to form or explosive spalling occurs is reported as the explosion resistance.

3 Results and discussion

3.1 Interaction between cement and other ingredients during storage of dry-mix

It is not an uncommon problem that castables deteriorate during storage. Often set-time gets seriously disturbed. A self-flowing castable based on SiC as aggregate, SHMP as dispersant and with 6 % cement (Ref-I in Tab. 1) was selected to investigate possible interactions between the individual ingredients during storage. The test set-up was to dry mix all the ingredients except for one specific ingredient each time. The dry-mix and the "missing" ingredient were stored separately in the climate room. Tests were done on freshly mixed samples and after 9 months storage in a climate room. The additive (SHMP) was stored in a sealed plastic box, i.e. not exposed to humidity.

The conditions in the climate room (70–80 % relative humidity at 20 °C) are rather harsh and the ageing process will be more extensive than would normally be experienced in "real life". However, the test set-up should give valuable indications of what is better or worse though. Fig. 1–2 show the self-flow and set-time of different mixes before and after nine months storage. All mixes show lower self-flow after storage than fresh mixes. The sample where the cement is the "missing" ingredient stands out and has a very low self-flow combined with a very short set-time. A plausible explanation might be that cement ages differently when mixed with microsilica or other fines. Pure cement reacts with humidity resulting in lumps, while in a castable dry-mix it is dispersed and coated i.e. the cement grains are spaced by the other ingredients so that cement lumps are avoided. Lumpy cement has a tendency of fast set, or even flash-set, when used in refractory mixes. The reason may be that in the cement lumps the surface gets only partially hydrated, the contact points are without hydrates, and these get exposed when the castable is mixed. The hydrates will accelerate setting by acting as nuclei for precipitation of the hydration products. In a premix with well distributed cement, the cement grain surface gets evenly hydrated and this hampers the dissolution of the cement. The result is long set. In this way the seemingly contradictory behaviour of cement ageing may be explained. The low flow may be caused by the quick set described above.

Overall, when the results in Fig. 1–2 are examined, it is the samples that were stored without additives that show least degradation. Obviously, the ageing is caused not only by individual components like cement and water but also by interactions between additives and one or several other ingredients of the castable. Influenced by humidity, the dispersant SHMP possibly reacts with cement and give longer set time than hydration of the cement surface alone.

To avoid additives from reacting with the cement they should be kept physically apart or

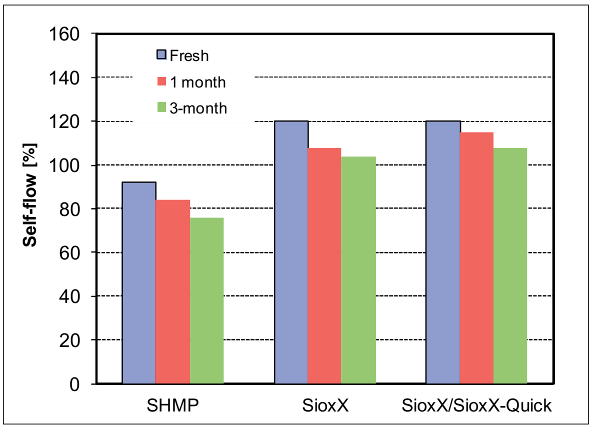

Fig. 3 Self-flow as a function of additive package and storage time

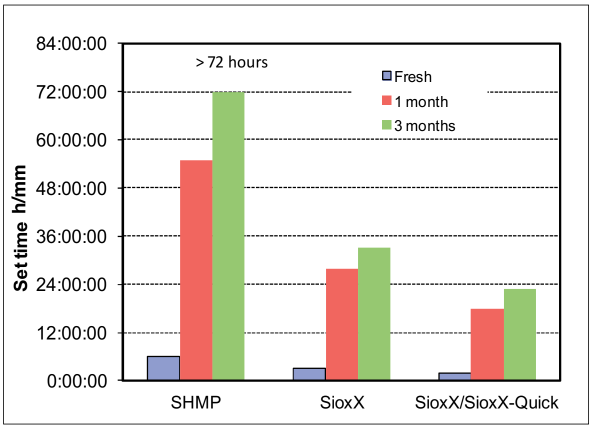

Fig. 4 Set-time as a function of additive package and storage time

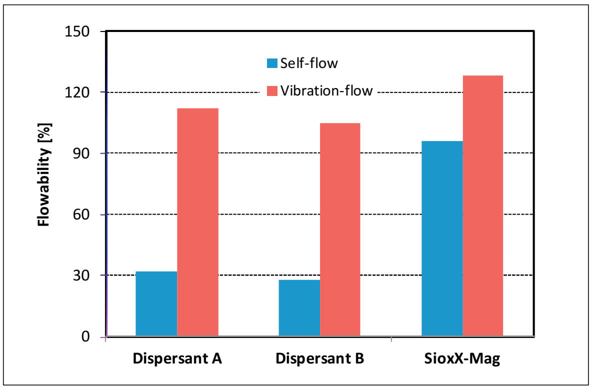

Fig. 5 Flow of MgO based castable with different dispersants

Fig. 6 Photo of cement-free MgO based castable with SioxX-Mag and microsilica

additives that do not react with cement should be used. The latter option probably rules out the phosphates, or at least most of them. Other organic additives and dispersants do probably fulfil that criterion, provided they are not too hygroscopic. This is exemplified in the self-flowing SiC LCC where the SHMP is replaced by the novel dispersant system, SioxX/SioxX-Quick described in the following.

3.2 SiC LCC with SioxX/SioxX-Quick

In this series, SHMP is replaced by the novel additive package SioxX/SioxX-Quick. The castable compositions are shown in Tab. 1. The components were mixed and stored in paper bags for up to 3 months in the climate room. Based on previous experience three months in the climate room will have the same ageing effect as 6 to 12 months in regular (dry) warehouse conditions.

The results (Fig. 3) indicate that independent of the additive package the flow of all mixes degrades somewhat during the three months storage period. It is interesting to note an increase in self-flow from 92 to 120 % of the fresh sample when SioxX replaced SHMP and that the addition of SioxX-Quick did not influence flow negatively. As shown in Fig. 4 the premix with SHMP as dispersant turns out to be useless since it did not set even after three days. The addition of SioxX-Quick not only reduced the set time for fresh compositions, but also offset the ageing somewhat.

Based on our limited test program one should be careful to draw firm conclusions, but it seems fair to say that additive/cement interaction are minimised if the phosphate dispersant is replaced by SioxX and further improved by the combination of SioxX and SioxX-Quick.

3.3 MgO based gel-bonded castable using SioxX-Mag as dispersant

Dispersants play an extremely important role in basic castables. In this study, a microsilica gel-bonded MgO-based castable is produced to demonstrate the feasibility of making high-performance basic refractory castables by using the new additive package SioxX-Mag. For comparison, mixes with two other commercially available dispersants are presented. The compositions are given in Tab. 2.

As seen in Fig. 5 both mixes with dispersant A and B have a self-flow of ~30 % and the vibration-flow is ~110 %. At the same water addition (5,5 %) the mix with SioxX-Mag exhibits dramatic improved flow properties.

All samples made for mechanical strength and hot properties testing were crack-free during set and drying process, as exemplified in Fig. 6. For the sample in which Microsilica and SioxX-Mag were not used, as shown in Fig. 7, slaking was observed after dried at 110 °C for 24 h. This indicates that the addition of microsilica and SioxX-Mag may suppress the hydration of MgO and formation of brucite and subsequently avoid cracking. The set-mechanism and the interaction between fine MgO, microsilica and SioxX-Mag are not fully understood yet and further research is ongoing.

The cold modulus of rupture (CMOR) is plotted as a function of firing temperature in

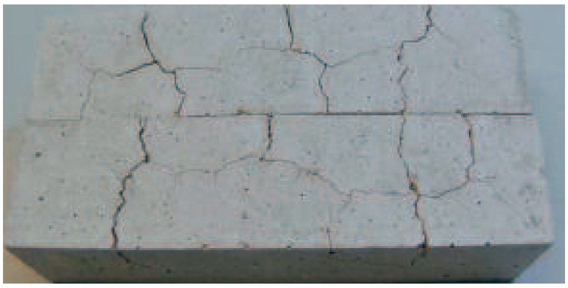

Fig. 7 Photo of cement-free MgO based castable without SioxX-Mag and without microsilica

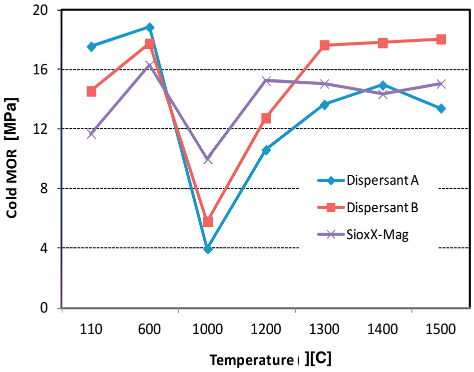

Fig. 8 Cold MOR as a function of firing temperature

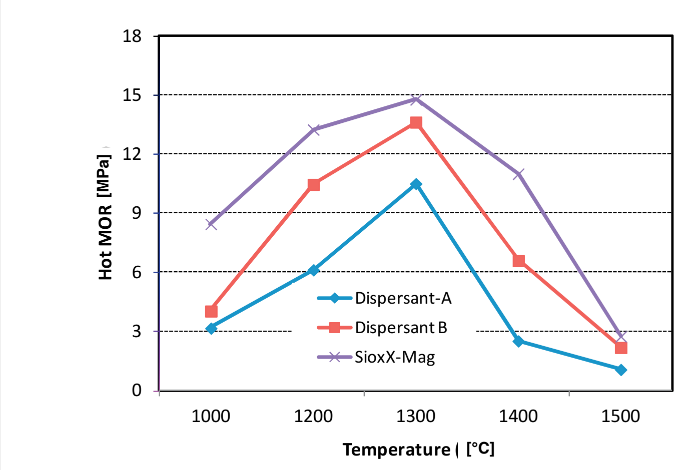

Fig. 9 Hot MOR as a function of test temperatures

Tab. 3 Explosion resistance according to Chinese Standard YB/T4117-2003. √ denotes that the sample passed the test; × denotes that the sample failed

Temp. [°C]	M1 (Dispersant-A)		M2 (Dispersant-B)		M3 (SioxX-Mag)	
	Wet	Dried	Wet	Dried	Wet	Dried
300	√	√	√	√	√	√
400	√	√	√	√	√	√
500	×	√	√	√	√	√
600	×	√	√	√	√	√
700			×		√	
800		√	×	√	×	√
1000		√		√	×	√

Fig. 8. The reason for the drop in strength from 600 to 1000 °C is not fully understood, but it may be connected to crystallization of an amorphous bond-phase. At higher temperatures strength is regained and this may be attributed to formation of forsterite (M$_2$S) from the reaction between MgO and microsilica starting at a temperature above approximately 1000 °C. However, the strength drop from 600 to 1000 °C seems to depend on the type of dispersant used. The specimens with SioxX-Mag show highest CMOR of ~10 MPa at 1000 °C, being about 70 % stronger than what is achieved using dispersant B. Apparently the type of dispersant not only affects the flowability and setting process of gel-bonded MgO castables, but also impacts the strength at intermediate temperatures.

Fig. 9 shows the hot modulus of rupture (HMOR) as a function of test temperature. For all mixes the development of HMOR is similar. From 1000° towards 1300 °C, HMOR increases and reaches a maximum value at 1300 °C. What is instereting is that, the HMOR for the castable with SioxX-Mag is consistently higher than the other castables.

It may therefore be concluded that the MgO based castable with SioxX-Mag as additive outperforms the other two castables in terms of HMOR. The reason for this is currently unclear but further research work is ongoing.

Tab. 3 summarizes the explosion test results of both "wet" and "dried" samples of gel-bonded MgO-based castables. The samples were cured at 100 % relative humidity at room temperature for 24 h before demoulding. The freshly de-moulded samples are labelled "wet" and samples dried at 110 °C for further 24 h are called "dried".

All "dried" samples show excellent explosion resistance and pass the test at 1000 °C. The good performance is attributed to the low amount of residual water in the bond phase after drying, and a stable bond phase during the firing process. When the "wet" samples were tested, best explosion resistance was achieved with SioxX-Mag (700 °C). This indicates that the dispersants play a role in of the bond phase formation, such as MgO hydration and the interaction between MgO and microsilica in the presence of water. The drying characteristics have been improved by using SioxX-Mag, therefore, fast firing of this type of castables is feasible.

4 Conclusions

In this paper, a SiC based self-flowing LCC with SioxX/SioxX-Quick was produced to investigate the interaction between cement and other ingredients during storage of dry-mix (shelf-life).

A gel-bonded MgO castable with SioxX-Mag was selected as example to illustrate how different dispersants influence the flowability, bond formation and hot properties of basic castables.

In a humid environment not only the cement hydrates, but the dispersants presumably enter into reactions with cement and/or other constituents in the castable premix during storage. The right choice of dispersant system is a good way to help control the ageing at "normal" moisture levels. This has been illustrated in this paper where SHMP was replaced by the SioxX/SioxX-Quick dispersant system resulting in both better flow and improved shelf life.

For basic castables, which are based on microsilica gel bond system, several attractive properties have been identified:

- Using SioxX-Mag together with Microsilica, slaking caused by brucite formation is suppressed and crack-free dried samples are made.
- MgO-SiO$_2$ bonded castables exhibit high green strength, e.g. CMOR is above 12 MPa after drying at 110 °C.
- MgO based castables exhibit very good placing properties combined with high hot strength and excellent explosion resistance.
- The bond phase contains only small amounts of chemically bound water, so once the free water is removed, the castable can be fired at very high heating rates.
- Substitution of commercially available dispersants with SioxX-Mag not only gave better flowability but also improved the hot properties and explosion resistance.
- Improved drying characteristics allowing fast firing of this type of castables.

References

[1] Evangelista, P.C.; Parr, C.; Revais, C.: Control of formulation and optimization of self flowing castables based on pure calcium aluminates. Refractories Applications and News 7 (2002) 14–18

[2] Karadeniz, E.; et al.: Properties of alumina based low-cement self flowing castable refractories, J. Europ. Ceram. Soc. **27** (2007) [2] 1849–1853

[3] Peng, H.; Myhre, B.: Effect of dispersants and raw materials on placing properties and shelf life of bauxite based low cement castables. Proc. 53rd Int. Coll. on Refractories, Aachen (2010) 62–66

[4] Peng, H.; Myhre, B.: Effect of bauxite fines and cement content on workability and high-temperature properties of bauxite based castables. Proc. UNITECR '09, Brazil (2009)

[5] Oliveira, I.R.; Pandolfelli, V.C.: Does a tiny amount of dispersant make any change to refractory castable properties? Ceram. Int. **36** (2010) [1] 79–85

[6] Studart, A.R.; et al.: Dispersion of microsilica-containing zero-cement highalumina castables. Amer. Ceram. Soc. Bull. **79** (2000) [2] 49–55

[7] Studart, A.R.; Gallo, J.; Pandolfelli, V.C.: Citric and polyacrylic acids as dispersants for high-alumina refractory castables. Amer. Ceram. Soc. Bull. **81** (2002) [4] 36–44

[8] Hidber, P.C.; Graule, T.J.; Gauckler, L.J.: Influence of the dispersant structure on properties of electrostatically stabilized aqueous alumina suspensions. J. Europ. Ceram. Soc. (1997) [17] 239–249

[9] Sandberg, B.; Mosberg, T.: Use of microsilica in binder systems for ultra-low cement castables and basic, "cement-free" castables. Advances in Refractories Technol. (1989) [4] 245–258

[10] Odegard, C.; et al.: Flow and properties of MgO based castables. XXXII Congreso ALAFAR Proc. (2004)

[11] Myhre, B.: Cement-free castables in the system $MgO-SiO_2$: The effect of bond phase modifiers on strength. Proc. of 93rd Annual Meeting. The Amer. Ceram. Soc. (1991)

[12] Odegard, C.; Feldborg, H.; Myhre, B.: Magnesia-silica-hydrate bonded MgO castables. Proc. of UNITECR '01, Mexico 2001

[13] Odegard, C.; et al.: $MgO-SiO_2-H_2O$ bonded MgO castables. Part 1: Effect on flow, set and hot properties when substituting microsilica with alumina in pumpable MgO based castables. 4th Int. Symposium on Refractories, Dalian, China 2003, 148–156

[14] Ghanbari Ahari, K.; Sharp, J.H; Lee, W.E: Hydration of refractory oxides in castable bond systems – I: alumina, magnesia, and alumina – magnesia mixtures. J. Europ. Ceram. Soc. **22** (2002) [4] 495–503

[15] 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

[16] 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

[17] Myhre, B.: Microsilica in alumina based ultra-low-cement castables. The effect of microsilica additions on flow. XXIII ALAFAR Congr., Puerto Vallarta, Mexico 1994

[18] Watanabe, Y.; et al.: Development and application of monolithic refractory containing magnesia clinker, Proc. of 2nd Int. Conf. of Refractories (REFRACTORIES'87 TOKYO), Japan 1987, 494–506

[19] Myhre, B.: Mullite formation in tabular alumina based refractory castables with hydraulic alumina as binder. Presented at the 97th Annual Meeting of the Amer. Ceram. Soc., Cincinnatti/OH, 1995

[20] Myhre, B.: Microsilica in alumina based ultra-low-cement castables. The effect of microsilica additions on flow. Proc. of the XXIII ALAFAR Congr., Mexico 1994

[21] Unpublished data. Application of SioxX/SioxX-Quick in various refractory castables. Internal report, Elkem, 2011