

DEVELOPMENT OF HIGH-PERFORMANCE NO-CEMENT REFRACTORY SHOTCRETE

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ABSTRACT

Microsilica-gel bonded no-cement refractory castable (NCC) draw increasing attention, not only because of easier handling, storage and transportation thanks to the “all-in-the-bag” solution, but also because of improved setting behaviour and higher green strength compared to silica-sol bonded NCC. The current work addresses the development of no-cement shotcrete using microsilica as a binder. The flow, setting-behaviour, mechanical properties, hot-properties of no-cement shotcrete were compared to low-cement shotcrete. The results demonstrate that the cement-free shotcrete not only exhibits good installation properties and low rebound, but also provides enhanced hot-properties. Microstructure and bond mechanism were investigated using SEM after firing at 1400 and 1500°C and confirm that mullite formation and less liquid phase are essential to give the excellent thermo-mechanical properties of microsilica-gel bonded shotcreted NCC.

Keywords: Microsilica-gel bond; no-cement castable (NCC), shotcrete

INTRODUCTION

A variety of installation techniques have been developed for different application areas of refractory castables, evolving from traditional casting using moulds, to time saving options such as conventional dry gunning and shotcreting (also sometimes referred to as wet-gunning)¹⁻². Shotcrete provides homogenous properties and does not generate dust, has very low rebound and high efficiency, with output up to 10-15 tonnes per hour. The shotcrete process is schematically described in Figure 1. The major features are: i) Water is added during a mixing step; ii) The installation process is continuous; iii) The wet-mix is pumped with high pressure pumps through a hose to its application area; iv) A set-accelerator is added at the end of the pipeline and distributed in pressurised air through the nozzle; v) the mix is sprayed onto a surface and consolidated. Contrary to dry gunning, the water content is strictly controlled in shotcrete.

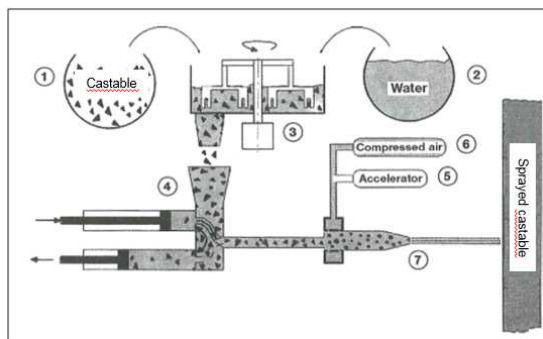


Fig. 1: Schematic drawing of the shotcrete installation process. Legend: 1=castable, 2=water, 3=mixer, 4=double-piston pump, 5=accelerator, 6=compressed air, 7=nozzle (illustration courtesy Caldeyrs)

Besides good shotcrete practice (such as selection of an appropriate pump, nozzle and experienced installation team) mix design (particle size distribution, dispersants and accelerator) is important to successfully install shotcrete. Although a number of research papers have been published during the last 30 years, most of them are focusing on equipment, accelerators or results from low-cement castable (LCC) and ultra-low cement castable (ULCC) prepared in the laboratory³⁻⁷. Furthermore, shotcreting of NCCs have not been widely applied, although the first shotcrete (wet-gunning) method for cement-free refractory castables was demonstrated by Iwasaki et al. in Japan⁸ in 1999. Recently, silica-sol bonded shotcreted NCCs have been reported used for blast furnace main troughs⁹ and in cement plants¹⁰. Colloidal silica bonded shotcrete not only exhibit good flowability and sufficient setting time but also provide better thermo-mechanical properties when compared to LCC. However, handling, storage and use of liquid silica-sol are logistic factors that must be dealt with, especially at lower temperatures.

Obviously, a technology based on a “dry-version” silica binder, using microsilica powder, is of great interest to further develop NCC. Recent reports disclose that a genuine bond based on microsilica coagulation is created, and that the setting of microsilica-gel bonded castables is caused by cations, a similar set mechanism to colloidal silica¹¹. The cations not only contribute to the reduction of the net repulsion effect of microsilica, but also bridge the negatively charged microsilica particles. If, e.g. calcium aluminate cement is used as coagulating agent, Ca^{2+} (and/or other polyvalent cations) released during dissolution of the cement will act at the negative sites on the microsilica surface to form a three-dimensional network of linked microsilica particles. Microsilica-gel bond not only provides similar advantages as silica-sol but also eliminates many of the drawbacks of a two-component system.

In this paper, shotcrete compositions of bauxite based NCCs were designed by using microsilica-gel as binder system in combination with specialty products. The tests were first carried out at lab-scale to check the workability and physical properties. Then several industrial-scale shotcrete trials were carried out in cooperation with industrial partners. Finally, the mechanical properties, hot-properties and bond mechanism were evaluated in comparison to shotcreted LCC.

EXPERIMENTAL

The particle size distributions (PSDs) were calculated using the EMMA program in order to achieve a good workability suitable for shotcrete¹². EMMA uses the Andreassen model and is widely used to evaluate and optimize particle packing in all types of castables. In the present study, the q-value was 0.27 for both NCC and LCC. Table 1 shows the compositions in detail. Bauxite, brown fused alumina (BSA) and calcined alumina with different particle size fractions were selected as aggregates. SioxX-Flow (Elkem, Norway) was used as specialty dispersant in the recipes. Based on the recipe of NCC-S, an additional mix labeled NCC-S* was made, to give an example where the initial set-time is controlled by adding an accelerator, for instance, additional 2% SioxX-Set. In the laboratory, the water addition for adequate flow was found to be 4.5% and 4.4% for NCC-

S and NCC-S*, respectively. The water addition was 5.0% for the LCC-S.

Tab. 1: Composition of bauxite based castables

%		NCC-S	NCC-S*	LCC-S
Bauxite	0-6mm	52	52	52
BSA 96	0-0,5mm	15,5	15,5	16
Calcined alumina	0-0,2mm	10	10	10
	0-0,045mm	5	5	5
	Fines	10	10	5
Calcium aluminate	70% Al ₂ O ₃	0,5	0,5	5
Drying agent	EMSIL-DRY	0,1	0,1	0,1
Microsilica	MS 971 U	6	6	6
Speciality products	SioxX-Flow	1	1	1
	SioxX-Set		2	
Water		4,5	4,4	5,0

At lab-scale, the dry components were mixed using a Hobart mixer for four minutes at 60RPM; water was added, and the castable was wet-mixed for an additional four minutes. Self-flow and vibration-flow were measured using the 50mm high flow-cone described in ASTM C230. The self-flow value is the % increase of the diameter of the fresh mix measured 90 seconds after removing the cone. Based on the results from the laboratory, NCC-S and LCC-S were chosen for further industrial-scale shotcrete trials. Mixes of approximately 500kg were prepared. The water addition was 4.5-4.8% for NCC-S and the LCC-S was shotcreted with 5.0-5.3% water. Panels were sprayed without complications, the mixes were easily pumped and responded well to the sodium silicate accelerator. The panels were prefired at 600°C before cutting. Fig. 2a and Fig. 2b show a panel and specimens cut from the panels. No lamination was observed in the centre of the panels and samples were cut for further characterisation. The cut specimens were fired at various temperatures before doing cold crushing strength (CCS), cold modulus of rupture (CMOR) and hot modulus of rupture (HMOR) measurement. The HMOR testing apparatus (Isoheat, UK) is equipped with a pre-heating chamber that keeps 10 samples at test temperature. The dried samples (25x25x150mm) were heated at 300°C/hr.

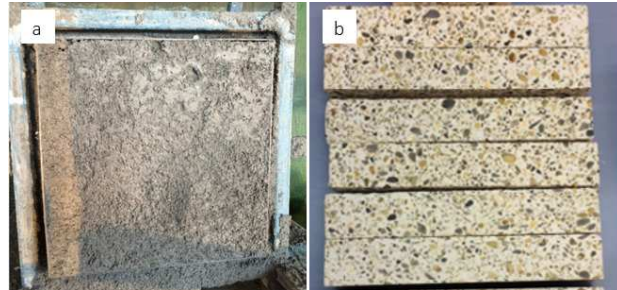


Fig. 2: Panel and cut specimens a) Panel (500x500x100mm) and b) Specimens (25x25x150mm) for HMOR test.

RESULTS AND DISCUSSION

Self- and vibration-flow values of lab-scale samples are shown in Fig. 3. The water addition is 4.4% and 4.5% for NCC-S and NCC-S*, respectively. The mix of NCC-S has slightly higher flow values than the others. The self-flow value of NCC-S is 52% and the vibration-flow is 112%.

Fig. 4 shows the ultrasonic velocity in the lab-scale mixes as a function of time from mixing. As stiffness and speed of sound are closely related, the increase in velocity indicates end of working time and initial set. As seen, the microsilica-gel bonded NCC-S has an extended working time whereas LCC-S exhibits 2-3hrs working time. Furthermore, the working time of NCC-S can be easily adjusted by using accelerator. The initial set-time decreases to 2-3 hrs when 2% SioxX-Set was added. This indicates the NCC-S* is able to be used

as castable at laboratory trial and demoulded after 24hrs curing for later properties evaluation. The results based on lab-cast specimens will be reported elsewhere.

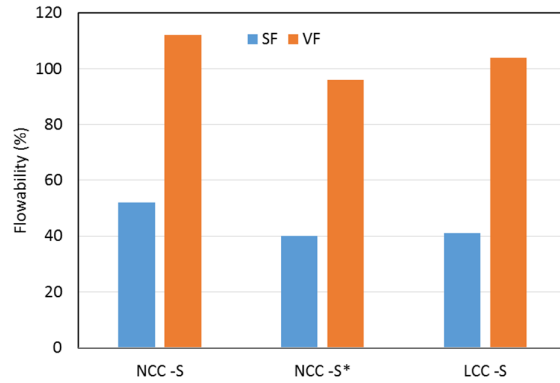


Fig. 3: Self-flow (SF) and vibration-flow (VF).

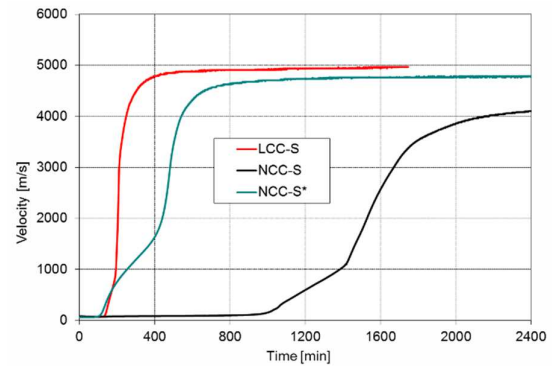


Fig. 4: Setting behaviour at 20°C. Ultrasonic velocity as a function of time.

The sprayed panels were prefired at 600°C before cutting, then the cut specimens were fired for 12hrs at 1000, 1200, 1300 and 1400°C before testing. The CCS and CMOR of both NCC-S and LCC-S are summarized in Fig. 5 and Fig. 6. In Fig. 5, it is surprisingly observed that the CCS of the NCC-S is higher than LCC at a firing temperature range of 600 to 1200°C. The CCS of microsilica-gel bonded NCC-S at 1000°C is ~85MPa, while the LCC-S only reaches ~60 MPa. The better performance could be attributed to 0.5% lower water addition in the NCC-S. At temperature above 1200°C, the CCS of both NCC-S and LCC-S are at the same level.

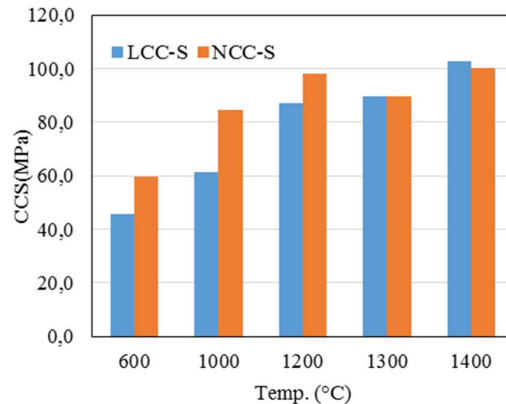


Fig. 5: CCS after firing at various temperatures.

As shown in Fig. 6, CMOR follows as expected the same trend as CCS. CMOR of the microsilica-gel bonded NCC-S reaches its highest value of 16MPa after firing at 1200°C.

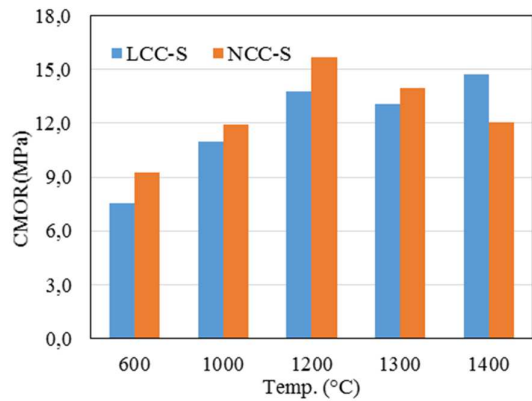


Fig. 6: CMOR after firing at various temperatures.

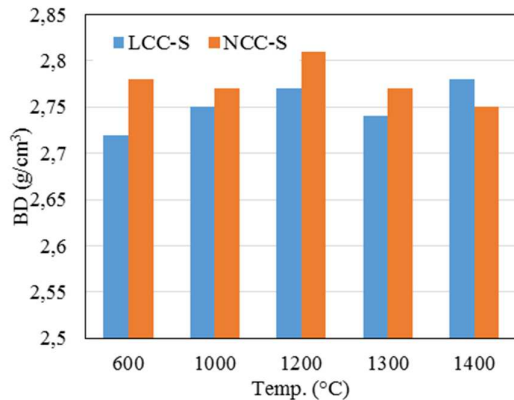


Fig. 7: Bulk density (BD) after firing at various temperatures.

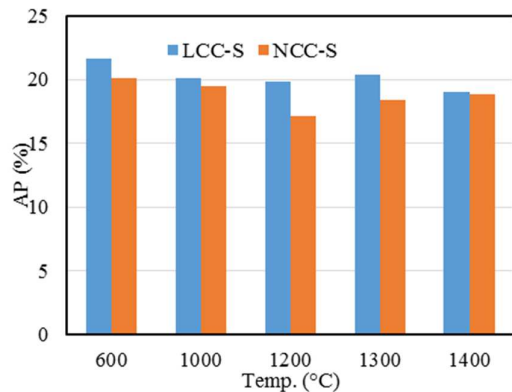


Fig. 8: Apparent porosity (AP) firing at various temperatures.

The bulk density and apparent porosity of the sprayed mixes after firing for 12 hours at 600, 1000, 1200, 1300 and 1400°C are summarized in Fig. 7 and Fig. 8. The bulk density of the sprayed samples of NCC-S is in the range of 2.75-2.81 g/cm³, slightly higher than that of LCC-S (in the range of 2.7-2.78 g/cm³). This is as expected due to mix composition and higher water addition in the LCC-S. As shown in Fig. 8, the porosity of both NCC-S and LCC-S decreases with the increase in firing temperatures and the porosity of the NCC-S is slightly lower than that of the LCC-S. The minimum porosity of the sprayed NCC-S is 17,2%, corresponding to a maximum bulk density of 2.81 g/cm³, while the porosity of the LCC-S is 19,8% at 1200°C corresponding to a bulk density of 2.78 g/cm³. The sprayed LCC-S exhibit slightly higher bulk density than the NCC-S, while the porosity is similar after firing at 1400°C. This is probably attributed to liquid formation where the liquid will fill the pores. This is probably also the reason behind the improved CCS and

CMOR for LCC-S after firing at 1400°C, as illustrated in Fig. 5 and Fig.6.

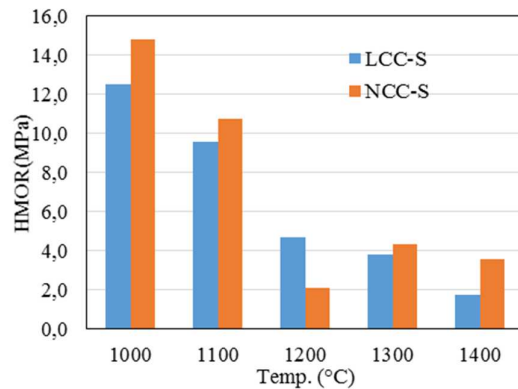


Fig. 9: HMOR at various test temperatures.

HMOR of the sprayed samples is shown in Fig. 9. Obviously, the development of HMOR of microsilica-gel bonded NCC-S is different from that of LCC-S. At 1000°C, the HMOR of NCC-S is ~15MPa, significantly higher than that of LCC-S. With increasing temperature up to 1400°C, HMOR for LCC-S drops continuously, probably due to the liquid formation between microsilica and cement. For NCC-S, alumina, silica and calcium (from the 0.5% cement added as coagulating agent) form a liquid phase around 1200°C. This causes the material to soften and the hot strength is significantly reduced. As seen in Fig. 9, the HMOR for NCC-S reaches its lowest value at 1200°C and then starts to increase. At 1300 and 1400°C, the NCC-S has improved hot strength compared to LCC-S. At 1400°C, the HMOR of NCC-S is ~3,5MPa, 100% higher than LCC-S. The improved HMOR is attributed to mullite formation, which is in line with our previous findings¹¹.

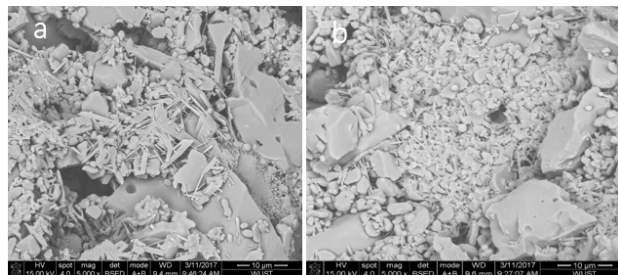


Fig. 10: SEM micrographs of etched fractured surfaces of sprayed specimens fired at 1200°C, a) LCC-S and b) NCC-S.

The microstructure of sprayed specimens of LCC-S and NCC-S after HMOR testing at 1200°C and 1400°C are shown in Fig. 10 and Fig. 11 respectively. As shown in Fig. 10, needle-like mullite is observed in the matrix of LCC-S while only trace amount of mullite is found in the microsilica-gel bonded NCC-S. This is probably attributed to the formed liquid phase from cement and microsilica at 1200°C that facilitates local mullite formation in LCC-S, which leads to higher HMOR compared to NCC-S (See Fig. 9). With an increase in temperature to 1400°C, numerous mullite crystals are observed in both LCC-S and NCC-S, as shown in Fig. 11. However, the difference is that the needle-like mullite in LCC-S are single crystals after the glassy phase has been etched away whereas the ones in NCC-S are interlocked and closely packed. This indicates that little liquid phase is formed in NCC-S and that a large amount of liquid is formed in LCC-S after firing at 1400°C. The mullite in LCC-S is embraced by the liquid phase and the strength deteriorates as soon as the liquid phase begins to form. On the contrary, for NCC-S, the needle-like mullite crystals provide strength by bridging the aggregates, forming a strong and highly refractory matrix.

