

Novel Binder Systems for No-Cement Castables: A Comprehensive Evaluation of Mechanical Strength and Hot Properties

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Abstract

Cement-free binders have recently attracted significant attention due to their rapid drying and superior high-temperature performance, including enhanced thermo-mechanical properties, refractoriness under load, and corrosion resistance, compared to low-cement castables (LCCs). Despite these advantages, conventional no-cement castables (NCCs) exhibit limited mechanical strength at intermediate temperatures (600 to ~ 1 000 °C). This study aims to develop innovative binder systems for NCCs, specifically targeting intermediate temperature applications, while also being suitable for high temperatures (> 1 300 °C). The research evaluated the flowability, setting behavior, and mechanical strength of NCCs incorporating novel cement-free binders, in comparison to conventional NCCs and LCCs. Additionally, hot properties such as hot modulus of rupture (HMOR), hot abrasion resistance (HAR), and refractoriness under load (RUL) were assessed. The results demonstrated that the novel binder system provided superior mechanical strength and improved hot properties at intermediate temperatures, surpassing conventional NCCs, while maintaining comparable performance at elevated temperatures. Notably, RUL results indicated that the novel binder facilitated sintering and/or mullite formation at a lower temperature (~ 800 °C) compared to the reference NCC (~ 1 300 °C), with reduced shrinkage after maximum expansion. Scanning electron microscopy (SEM) analysis confirmed that the novel binder influenced both the temperature and morphology of mullite formation, contributing to the observed improvements.

Keywords: No-cement refractory castables, microsilica-gel binder, intermediate-temperature applications, mullite formation.

I. Introduction

Refractory castables are extensively employed across various high-temperature industries, including steel, cement, glass, copper, nickel, and aluminum production. Recent advancements in refractory castables have been driven by industry demands, particularly from the iron and steel sector. Over the past four decades, research and development efforts in refractory castables have primarily focused on the following aspects^{1–4}:

- i. New materials and binders: Innovative exploration of new materials and binders has significantly enhanced performance while reducing the CO₂ footprint, thereby mitigating the overall environmental impact.
- ii. Manufacturing/monitoring techniques: Innovations in manufacturing processes have improved refractory castable properties, while advancements in monitoring technology during use have extended their service life and prevented catastrophic failures.
- iii. Installation methods: New installation approaches have shortened installation time, provided energy savings, and enhanced castable performance.

The development in binder systems has been one of the most important aspects in the advancement of refractory castables. Calcium aluminate cement is still by far the most

widely used hydraulic binder in unshaped refractories due to its fast setting, high mechanical strength, and good resistance to a wide range of chemically aggressive environments. Based on their CaO content, refractory castables can be classified into three types according to ISO1927: low-cement castables (LCCs) with 1.0 % to 2.5 % CaO, ultra-low cement castables (ULCCs) with 0.2 % to 1.0 % CaO, and no-cement castables (NCCs) with up to 0.2 % CaO. However, the CaO content in the binder system affects the amount of liquid phase formed during the sintering process with the presence of SiO₂, which can impact the strength, density, and microstructure of the castables. The major challenges facing cement-bonded refractory castables can be summarized as follows:

- i. Ageing: Due to the interaction between the dry mix and moisture from the environment.
- ii. Explosive spalling: During dry-out caused by the removal of free water and dehydration of hydrate phases.
- iii. Low refractoriness at high temperatures: Due to liquid phase formation in the presence of silica.
- iv. Volume expansion in systems without SiO₂: Resulting from both CA₂ and CA₆ formation at elevated temperatures, leading to crack formation and/or a less dense microstructure in alumina spinel-containing castables.

A notable trend in binder development for refractory castables is the shift towards reducing cement content

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to meet industrial demands, improve high-temperature properties, and enhance dry-out behaviors to reduce explosion risks and save energy, thereby mitigating the environmental impact. Consequently, the development of binders from low-cement to ultra-low and no-cement has been extensively investigated in recent years.

Alternative cement-free binders such as colloidal silica^{5,6}, colloidal alumina⁷, hydratable alumina⁸, sub-micron alumina⁹, microsilica¹⁰, phosphates¹¹, and geopolymers¹² have been explored to replace cement and reduce the amount of CaO in the binder system. Colloidal silica is a commercially used cement-free binder, but its use is limited by frost sensitivity during installation, storage and transportation, long setting times, complex behavior, and inadequate green strength. Hydratable alumina and colloidal alumina are employed to mitigate volumetric expansion in refractory castables containing alumina pre-sintered and/or *in-situ* spinel, where the addition of silica is undesirable. However, hydratable alumina encounters challenges in no-cement castables due to prolonged mixing times and high-water demand, while colloidal alumina suffers from limited addition and workability issues. Subsequently, submicron alumina has been investigated as a drying binder to replace colloidal and hydratable alumina, overcoming their disadvantages while retaining their benefits. Recently, geopolymers have demonstrated several advantages over CAC, including faster setting times, reduced risk of damage during drying, and optimized mechanical behavior. Nonetheless, their application is restricted to insulation materials due to the inherent low-melting-point phases.

Microsilica has indeed garnered attention as a dry-version, cement-free binder to replace colloidal silica, owing to its environmental advantages and exceptional thermomechanical properties^{13,14}. This green binder shows promise in significantly reducing the CO₂ footprint of refractory castables. However, the utilization of refractories employing microsilica-gel as the sole binder is limited due to extended setting times and moderate to low green strength on demolding. To address these limitations, a cement-free dry binder based on the chemical composition of SiO₂-Al₂O₃ (commercially known as SioxX[®]-Zero) has been developed^{15,16}. This binder utilizes high-grade microsilica as a carrier, offering precise setting times, rapid attainment of green strength, and improved hot properties. The utilization of such a dry-silica binder system maintains the advantages of a silica bond system, which contains minimal cement content and demonstrates superior high-temperature properties compared to low-cement castables (LCCs)^{14–16}.

However, the mechanical strength of such cement-free refractory castables at intermediate temperatures (600 to 1 000 °C) may often be lower than that of low-cement-bonded castables. The exploration of alternative binders to enhance the performance and longevity of no-cement castables to meet the requirements of industrial applications at intermediate temperatures, such as aluminum, petrochemicals, and power plants, has drawn great attention. This study focuses on two novel microsilica-gel-bonded binders engineered to cover the application ar-

reas that the existing one does not. These binders aim to achieve high mechanical strength at intermediate temperatures (600 to 1 000 °C), being comparable with low-cement castables, while preserving similar high strength at temperatures exceeding 1 400 °C, akin to no-cement castables containing the existing binder SioxX[®]-Zero (SZ). The investigation encompassed various aspects of these new binder systems, including flowability, setting characteristics, mechanical properties, and high-temperature performance metrics such as Hot Modulus of Rupture (HMOR), Hot Abrasion Resistance (HAR), and Refractoriness Under Load (RUL) of the castables. The strategic application of the appropriate binder system tailored to specific industrial segments holds the potential to elevate operational efficiency and performance in industrial processes.

II. Experimental

(1) Mix design

The particle size distributions (PSDs) of all the mixes were determined using software (called EMMA, developed by Elkem), which is based on the Andreassen model¹⁷. This computational tool is widely utilized for evaluating and optimizing the packing of particles in castables. The q-value was set to 0.25 for all the mixes.

Tabular alumina in different size fractions (3–6 mm, 1–3 mm, and 0–1 mm, from Altmatis, Germany) was utilized as aggregate, while microsilica (Microsilica[®] 971, Elkem, Norway) and calcined alumina fines (D₅₀ of 3–4 µm, Altmatis, Germany) were utilized as fines. The binder systems included three cement-free binder systems and one low-cement binder. In the cement-free binder system, 0.5 wt% calcium aluminate cement (CAC) with 70 % alumina was used as a coagulating agent. Table 1 presents the overall compositions of refractory castables. Cement-free castables containing SioxX[®]-Zero and low-cement castables were used as reference samples.

The three cement-free binders investigated were: (i) SioxX[®]-Zero (SZ, Elkem, Norway) with a mass ratio composition of Al₂O₃/SiO₂ approximately ranging from 0.48 to 0.55, (ii) SioxX[®]-Ten, and (iii) SioxX[®]-Ten PLUS (ST and STP, respectively, Elkem, Norway), with a mass ratio composition of Al₂O₃/SiO₂ of around 0.43–0.48. The SioxX[®]-Zero binder has been on the market for nearly a decade and is designed for use at temperatures exceeding 1 400 °C. In contrast, the latter two binders were introduced onto the market in September 2024, with a primary focus on enhancing mechanical strength at intermediate temperature ranges: 800 °C – 1 100 °C for SioxX[®]-Ten (ST), and 600 °C to 900 °C for SioxX[®]-Ten PLUS (STP). All three cement-free binders are based on a microsilica-gel bond, utilizing a dry version of silica as the carrier material. This formulation overcomes the limitations associated with colloidal silica binders, such as frost sensitivity, while retaining advantages like rapid dry-out and excellent thermal properties compared to cement binders. The recommended dosage for the proposed cement-free binders was 3 wt%. In the case of low-cement castables (LCC), 5.0 wt% calcium aluminate cement (CAC) was employed as a binder, with water addition set at 4.35 % for all mixtures.

Table 1: Overall composition of tabular-alumina-based refractory castables.

Raw materials (mass%)		NCC-SZ	NCC-ST	NCC-STP	LCC
Aggregates	Tab Alumina (0–5.0 mm)	82.5	82.5	82.5	82.5
Matrix	Microsilica® 971	5.0	5.0	5.0	5.0
	CAC (70% Al ₂ O ₃)	0.5	0.5	0.5	5.0
	Alumina fines	9.0	9.0	9.0	7.0
Binder	SioxX®-Zero (SZ)	3.0			
	SioxX®-Ten (ST)		3.0		
	SioxX®-Ten PLUS (STP)			3.0	
Additives	SioxX®-Flow				1.0
Drying agent	EMSIL-DRY®	0.1	0.1	0.1	0.1

(2) Experimental procedures and characterizations

The dry components were mixed for 4 minutes at 60 RPM using a Hobart mixer. Water was subsequently added, and the castable was wet-mixed for an additional 4 minutes. The self-flow and vibration-flow properties of the castable were measured using the flow-cone with a height of 50 mm as described in EN ISO 1927–4. The self-flow value was determined as the percentage increase in diameter of the fresh mix, measured 90 seconds after removing the cone.

The wet mixes were cast into molds with different dimensions for further characterization:

- 40 mm x 40 mm x 160 mm for Cold Modulus of Rupture (CMOR) and Cold Crushing Strength (CCS), and
- 25 mm x 25 mm x 150 mm for Hot Modulus of Rupture (HMOR).

Cylinders with a diameter of 50 mm and a central bore of 12.5 mm diameter were also produced, following DIN EN ISO 1893:2008 guidelines for Refractoriness Under Load (RUL). The molds were kept at 20 °C and > 90 % RH for 24 hours before demolding. The HMOR testing apparatus (Isoheat, UK) is equipped with a pre-heating chamber that keeps ten samples at test temperature. The dried samples were heated at 300 K/h. The Refractoriness Under Load (RUL) test was carried out on cylinders with a height of 50 mm. The constant load on the test samples was 0.2 MPa, and the maximum testing temperature was 1 800 °C. The thermal expansion was recorded during heating.

The Hot Abrasion Resistance (HAR) tests were conducted in accordance with ASTM C704 at temperatures of 815 and 1 100 °C, with 1 kg of silicon carbide grain injected into the circuit. Prior to the abrasion test, the samples were pre-fired at temperatures of 815 °C and 1 100 °C for 12 h. The dimensions of the specimens used in the abrasion resistance test were 115 mm x 115 mm x 65 mm. The bulk density of the samples was calculated by measuring and weighing them before conducting the abrasion resistance test. The initial dimensions and mass of the samples were measured before and after the abrasion resistance test. Finally, the volumetric losses (in cm³) were calculated to evaluate the abrasion resistance test of the samples.

(3) Scanning Electron Microscope (SEM)

A Scanning Electron Microscope (SEM, EVO-10 model from Zeiss, Germany) with energy-dispersive X-ray spectroscopy (EDS, Xplore30 model from Oxford, Britain) was used to investigate the microstructures of the samples after firing at 815 and 1 200 °C. Before the microstructures were examined, the polished surfaces of the samples were etched in an HF solution to remove the glassy phase. This allowed for a more detailed examination of the microstructure of the refractory castables and provided insights into the distribution and composition of the different phases within the samples.

III. Results and Discussion

(1) Flowability and setting and hardening process

The values for self-flow and vibration-flow were measured and are presented in Fig. 1. The results indicate that all NCC specimens exhibited excellent self-flow and vibration-flow properties, with values of approximately 60 % and 110 to 120 %, respectively, at a water dosage of 4.35 wt%. In contrast, the LCC specimens at the same water dosage exhibited a significantly lower self-flow value of 20 %, which is probably due to the hydration of calcium aluminate consuming part of the water, leaving less water available for mixing the material.

As gel-bonded castables do not provide accurate temperature readings using exothermic curves, ultrasound propagation was utilized to monitor the setting and hardening process. The stiffness and speed of sound are closely linked, and an increase in velocity indicates the end of working time and the initial set. Fig. 2 presents the ultrasonic velocity as a function of time during curing for all specimens. It was noticed that all NCCs exhibited a similar ‘defined’ setting process, similar to LCC, where the initial start time was approximately 2.0 hours, when the ultrasonic velocity increased. After roughly 8 to 10 hours, it flattened out, indicating the final set-time. It is worth noting that the term ‘defined’ is used here because once the castable begins to set, the strength development is rapid. However, the setting behavior of LCC is faster due to the cement hydration compared to NCC.

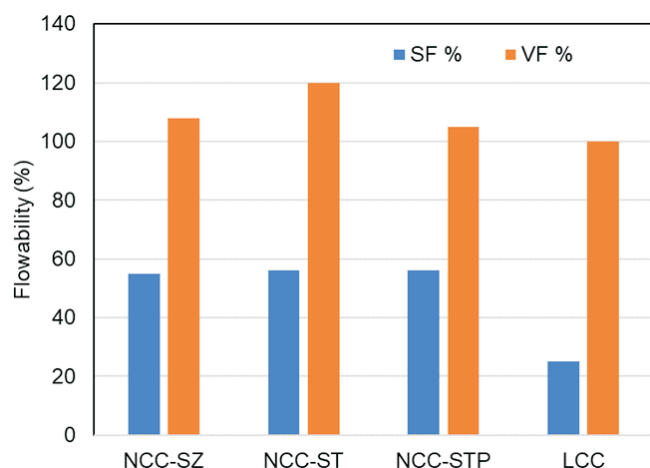


Fig. 1: Self-flow (SF) and vibration-flow (VF) of refractory castables containing different binders.

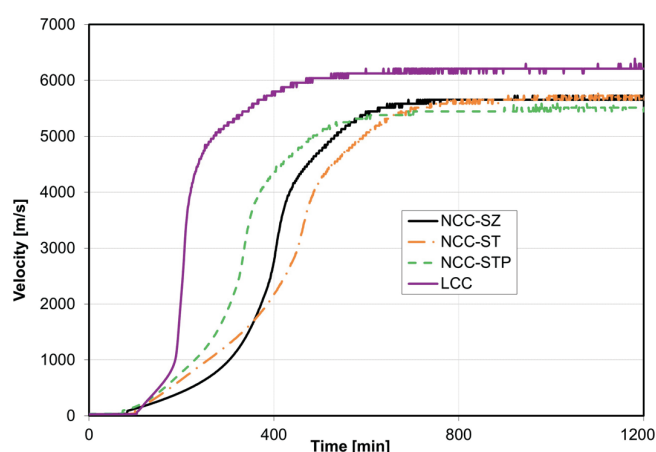


Fig. 2: Setting behavior of refractory castables containing different binders at 20 °C. Ultrasonic velocity as a function of time.

(2) Mechanical strength

The Cold Modulus of Rupture (CMOR) and Cold Crushing Strength (CCS) were measured for all samples after different treatments, as outlined in Fig. 3 and Fig. 4, respectively.

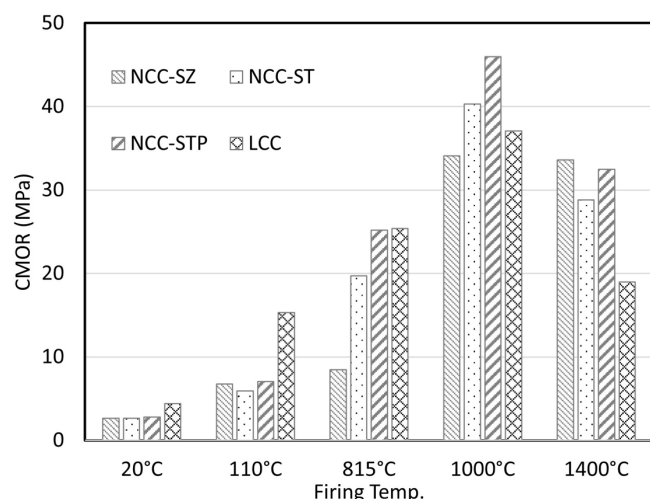


Fig. 3: Cold Modulus of Rupture (CMOR) of refractory castables with varying binders after firing at different temperatures. .

As depicted in Fig. 3, all NCC samples displayed similar green strength upon demolding, as evidenced by corresponding CMOR (Cold Modulus of Rupture) values ranging from approximately 2.0 to 3.0 MPa. Following a 24-hour drying period at 110 °C, the CMOR values increased to around 7.0 MPa, which remained below that of LCC. Nonetheless, upon a further increase of the firing temperature to 815 °C, the mechanical strength of all specimens increased proportionally with the rise in firing temperature. Specifically, among the NCC specimens, those containing the novel binder system, NCC-ST and NCC-STP, demonstrated significantly higher CMOR values of approximately 19.7 MPa and 25.2 MPa, respectively. These values were comparable to those of LCC. Conversely, the reference sample (NCC-SZ) displayed a CMOR value of merely 8.5 MPa. Upon a further increase of the firing temperature to 1000 °C, NCC-ST displayed the highest strength among the samples, followed by NCC-STP, NCC-SZ, and LCC. Finally, at 1400 °C, all NCC specimens demonstrated comparable CMOR values of approximately 30 MPa, which were much higher than that of LCC with a CMOR of 19 MPa. These findings emphasize the significant impact of the binder type on sintering temperature and ceramic bonding formation.

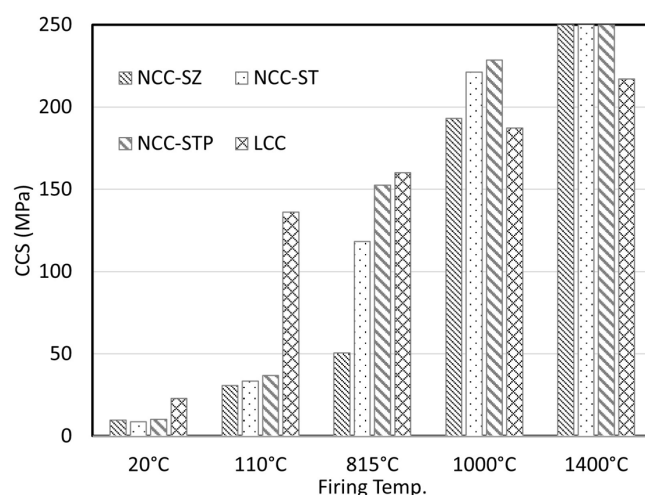


Fig. 4: Cold Crushing Strength (CCS) of refractory castables with varying binders after firing at different temperatures.

The development trend in Cold Crushing Strength (CCS) of refractory castable specimens is similar to that observed for the CMOR, as illustrated in Fig. 4. After a 24-hour drying period at 110 °C, the CCS values for all NCCs were in the range of 30 to 40 MPa, which was sufficient for installation purposes but significantly lower than the CCS of LCC. At 815 °C, the NCC-ST and NCC-STP specimens, incorporating novel binders, exhibited high strength, achieving CCS values comparable to LCC, approximately 150 MPa. In contrast, NCC-SZ displayed a CCS of 50 MPa. Upon further increase of the firing temperature to 1400 °C, all NCCs demonstrated superior strength compared to that of the LCC.

The mechanical strength of CMOR and CCS, as described above, increases with higher firing temperatures, mainly due to enhanced sintering, phase transformations, and improved bonding. This is likely attributed to the binder system (ST and STP) used in these samples, which

promotes better sintering and ceramic bonding formation at intermediate temperature range (600 to 1 000 °C). Microstructure characterization of these samples was carried out to understand the mechanism behind the improved mechanical strength at intermediate temperatures, with results to be presented in the following paragraphs.

(3) Hot Modulus of rupture (HMOR)

The HMOR parameter is of utmost importance with regard to selecting materials for high-temperature applications, as it provides valuable insight into the material's ability to maintain structural integrity and withstand stress at elevated temperatures. Fig. 5 depicts the HMOR of refractory castables at various test temperatures from 600 to 1 500 °C.

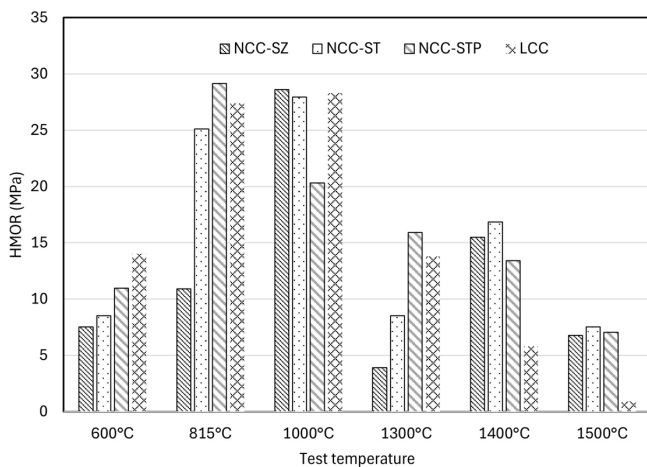


Fig. 5: Hot Modulus of Rupture (HMOR) of refractory castables with varying binders at different test temperatures.

At a temperature of 600 °C, NCC-ST and NCC-STP had already exhibited improved HMOR compared to NCC-SZ, although still lower than LCC. As the temperature increased to 815 °C, both NCC-ST and NCC-STP exhibited a significant enhancement in hot modulus of rupture (HMOR) compared to NCC-SZ, achieving strengths comparable to low-cement castables (LCC). As the temperature increased to 1 000 °C, the NCC-STP mixture exhibited the lowest HMOR value among the samples, indicating the onset of liquid formation, potentially the initial start of mullite formation. At 1 300 °C, the reference NCC-SZ sample displayed the lowest HMOR value, while NCC-ST and NCC-STP showed increasing HMOR values. This behavior is attributed to substantial mullite formation in NCC-ST and NCC-STP, whereas mullite formation in NCC-SZ began to take place from the liquid phase at 1 300 °C. Obviously, the incorporation of binder systems, SioxX®-Ten (ST) and SioxX®-Ten PLUS (STP), facilitated liquid and mullite formation at lower temperatures compared to NCC-SZ. Notably, at elevated temperatures of 1 400 °C and 1 500 °C, as the mullite formation process had completed, all NCC specimens showed excellent hot properties compared to LCC. The HMOR of NCC-ST and NCC-STP with novel binder systems were approximately 14–15 MPa and 7.0 MPa, respectively. These values are significantly higher than those of LCCs, with HMOR values of around 6.0 MPa and 0.7 MPa at 1 400 °C and 1 500 °C, respectively.

The obtained HMOR results provide compelling evidence that NCC-ST and NCC-STP with novel binder systems exhibit superior performance compared to NCC-SZ within intermediate temperature ranges (600 to 1 000 °C) and at 1 300 °C, achieving strength comparable to LCC. At temperatures ranging from 1 400 °C to 1 500 °C, the performance of NCC-ST and NCC-STP is comparable to that of NCC-SZ, yet significantly superior to LCC. These findings underscore the potential of innovative cement-free binder systems to enhance mechanical strength and thermal stress resistance in NCCs at intermediate temperatures, while maintaining comparable hot properties at elevated temperatures, such as 1 400 °C and 1 500 °C. The improvement in refractory castable performance and durability across diverse industrial applications is highly significant.

(4) Abrasion resistance test

Refractory materials with high abrasion resistance are essential in various industrial applications, particularly in petrochemical cracking units. Traditionally, abrasion resistance is assessed at room temperature. However, evaluating hot abrasion resistance at elevated temperatures more accurately reflects actual operating conditions. Fig. 6 illustrates the hot abrasion loss of all specimens, presented as volumetric loss in cm³ and tested at 815 °C and 1 100 °C. At both test temperatures, NCC-ST and NCC-STP demonstrated superior abrasion resistance compared to NCC-SZ and LCC. Particularly, NCC-STP exhibited the best abrasion resistance, showing the lowest volumetric loss values of approximately 0.19 cm³ and 0.21 cm³ after firing at 815 °C and 1 100 °C, respectively.

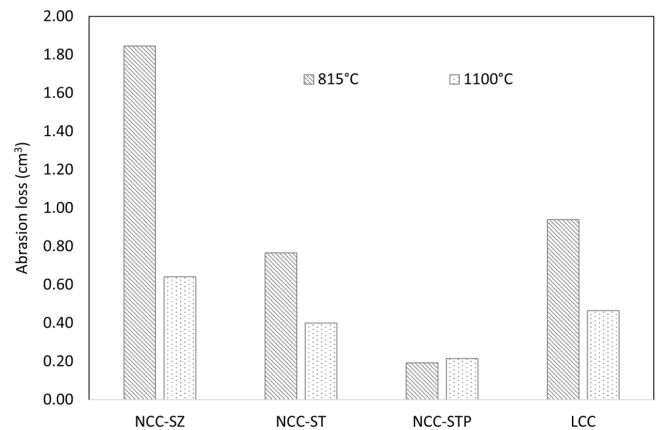


Fig. 6: Volumetric loss (cm³) of refractory castable with varying binders after abrasion test at various temperatures. a) 815 °C and b) 1 100 °C.

Moreover, most specimens, except NCC-STP, exhibited decreased volumetric loss at the higher firing temperature of 1 100 °C compared to 815 °C. This enhancement in wear resistance can be attributed to the sintering effect and ceramic bonding resulting from the development of new phases, such as mullite. The exceptional abrasion resistance of NCC-ST and NCC-STP can be attributed to their elevated mechanical strength, with NCC-STP exhibiting a CMOR of 25.7 MPa, which is 200 % higher than that of NCC-SZ after firing at 815 °C (Fig. 3). The enhanced abra-

sion resistance of NCC-ST and NCC-STP is likely connected to their increased mechanical strength at intermediate temperature ranges. This correlation highlights that both mechanical strength and abrasion resistance are significantly influenced by factors such as porosity, density, presence of a liquid phase, mineral phases, and overall material quality.

(5) Refractoriness Under Load (RUL) of refractory castables

To understand the effect of the binder system on the behavior of refractory materials under high temperatures and mechanical loads, the Refractoriness Under Load (RUL) test was carried out on the samples after heat treatment at both 200 °C and 1 500 °C for 24 hours.

Fig. 7 summarizes the Refractoriness Under Load (RUL) results after drying at 200 °C. These results allowed us to investigate the sintering process and phase transformations during the initial heating cycle. For all NCC specimens, regardless of the binder system, the heating process can be divided into three distinct stages, as exemplified by the NCC-SZ specimens:

- Stage I (Room Temperature to 1 000 °C): Expansion continues with increasing temperature, attributed to the thermal expansion of the material.
- Stage II (1 000 °C to 1 350 °C): Initial shrinkage begins due to sintering and phase transitions.
- Stage III (1 350 °C to 1 700 °C): Initial deformation occurs at around 1 350 °C due to the formation of liquid phases and continues until around 1 400–1 500 °C, followed by a ‘plateau’ observed up to 1 700 °C. This plateau marks significant structural changes within the material. According to early research, this plateau indicates the formation of *in-situ* mullite, resulting from the reaction between Al_2O_3 and SiO_2 ¹⁵.

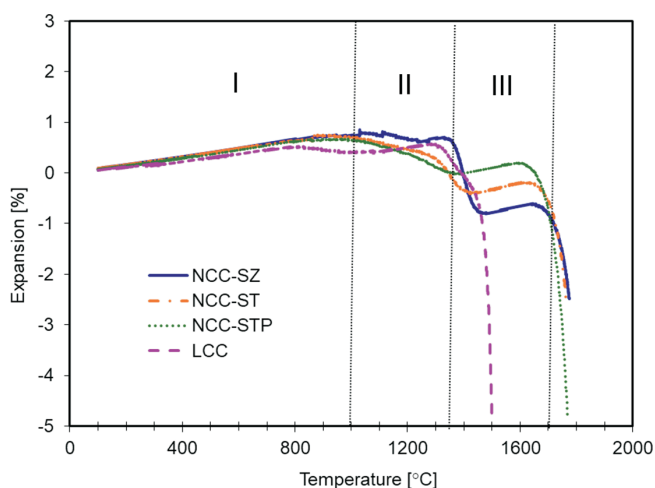


Fig. 7: Refractoriness Under Loading (RUL) of refractory castable with varying binders after drying at 200 °C for 24 h.

Even though the NCC-ST and NCC-STP exhibited a similar three-stage heating process as NCC-SZ, it was noticed that the temperatures for sintering, liquid formation, and phase transitions were in lower temperature ranges. Furthermore, the degree of deformation during Stage II of the specimens of NCC-ST and NCC-STP was much smaller than that of NCC-SZ before reaching the ‘halt-

ed stage with a plateau indicating mullite formation.’ This could explain why NCC-ST and NCC-STP demonstrated improved cold and hot strength at intermediate temperatures, such as around 815 °C (Fig. 3 and Fig. 4). In contrast, the RUL results of LCC after heat treatment at 200 °C showed different behavior. Normal expansion from room temperature to approximately 800 °C was observed due to the thermal expansion of the materials. This was followed by initial shrinkage caused by the dehydration of cement hydrates and sintering. Upon further heating, deformation began after maximum expansion at approximately 1 300 °C and continued with increasing temperature, reaching up to ~5.0 % at 1 500 °C.

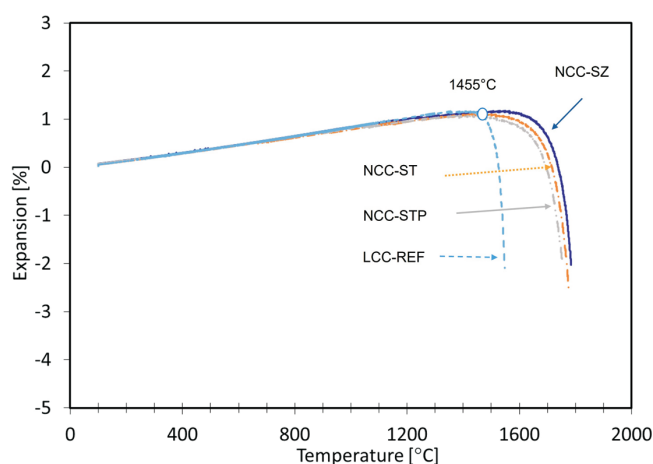


Fig. 8: Refractoriness Under Loading (RUL) of refractory castable with varying binders after firing at 1 500 °C for 24 h.

Fig. 8 presents the RUL results of all specimens after pre-firing at 1 500 °C for 24 hours. Sintering, liquid formation, and mullite formation were completed before testing. Consequently, the typical mullite formation, characterized by initial deformation around 1 350 °C followed by a plateau in the RUL curve, was no longer observed. The pre-firing temperature of 1 500 °C shifted the softening point from around 1 350 °C to the range of 1 600–1 700 °C for NCC specimens. The NCC-ST and NCC-STP specimens exhibited slightly lower softening temperatures but comparable values, indicating that novel binder systems promote mullite formation at lower temperatures than the reference NCC-SZ sample while achieving comparable hot properties. In contrast, LCC specimens softened at around 1 450 °C and collapsed with further temperature increases, similar to samples dried only at 200 °C.

The RUL results highlight the significant impact of binder types on thermal stability, sintering, and phase transitions during heating, leading to differences in the properties of the castables. Notably, the presence of typical ‘plateaus’ in expansion curves, indicating mullite formation at elevated temperatures, was observed for all NCC specimens after heat treatment at 200 °C for 24 hours. In contrast, this phenomenon was not observed in LCCs. This discrepancy can be attributed to the absence of mullite formation or the dispersion of mullite in liquid without reinforcement in LCCs, as elucidated by the ternary phase diagram of the Al_2O_3 - SiO_2 -CaO system ^{18,19}.

To enhance mullite formation and optimize performance under high-temperature conditions, it is crucial to strategically formulate the bond phase composition of alumina-silicate castables within two key compatibility triangles of mineral phases: (i) corundum, anorthite, and mullite, or (ii) mullite, anorthite, and silica. Binder compositions outside these compatibility regions do not facilitate favorable mullite formation and may result in its dissolution into the liquid phase during heating. In the case of low-cement castable (LCC) specimens containing 5 wt% calcium aluminate cement as a binder, a substantial portion of silica is consumed at elevated temperatures to form a liquid phase. This consumption significantly reduces the availability of silica for mullite formation. Consequently, the LCCs demonstrate inferior performance compared to no-cement castables (NCCs)

(6) Microstructure development and mullite formation analyzed with SEM and EDS

To elucidate the sintering process and associated phase transitions, such as mullite formation in no-cement castables (NCCs) with various binders during heating, the microstructural development of specimens after firing at different temperatures was examined using Scanning Electron Microscopy (SEM) coupled with Energy-Dispersive Spectroscopy (EDS). Fig. 9 and Fig. 10 present the SEM micrographs and EDS analyses of the etched polished surfaces of NCC-SZ and NCC-STP after firing at 815 °C, 1 200 °C, and 1 400 °C, respectively.

For the NCC-SZ specimen, corundum was detected alongside microsilica after firing at 815 °C, with no evidence of mullite formation. At 1 200 °C, the phase morphology remained largely unchanged, with no needle-like mullite phases observed, although EDS indicated the presence of mullite particles. In contrast, NCC-STP exhibited notable differences. At 815 °C, numerous sponge and whisker-like phases were observed, indicating the onset of the sintering process and transient liquid formation, with whisker phases as precursors to mullite formation. At 1 200 °C, numerous small needle-like mullite phases were formed, enhancing the thermal properties of NCC-STP at intermediate temperatures (600 to 1 200 °C) compared to NCC-SZ. At 1 400 °C, numerous needle-like mullite crystals were observed in both NCC-SZ and NCC-STP, but their morphologies differed. NCC-SZ exhibited interlocked and closely packed needle-like mullite, whereas NCC-STP contained coarser and longer mullite crystals, partially interlocked after the glassy phase was etched away. This suggests less liquid phase formation in NCC-SZ than in NCC-STP. Additionally, some mullite in NCC-STP is likely encapsulated by a small amount of liquid phase, resulting in slightly lower strength compared to NCC-SZ, though still comparable. In both cases, the needle-like mullite crystals formed an interlocked microstructure, providing strength by bridging the aggregates and forming a robust and highly refractory matrix.

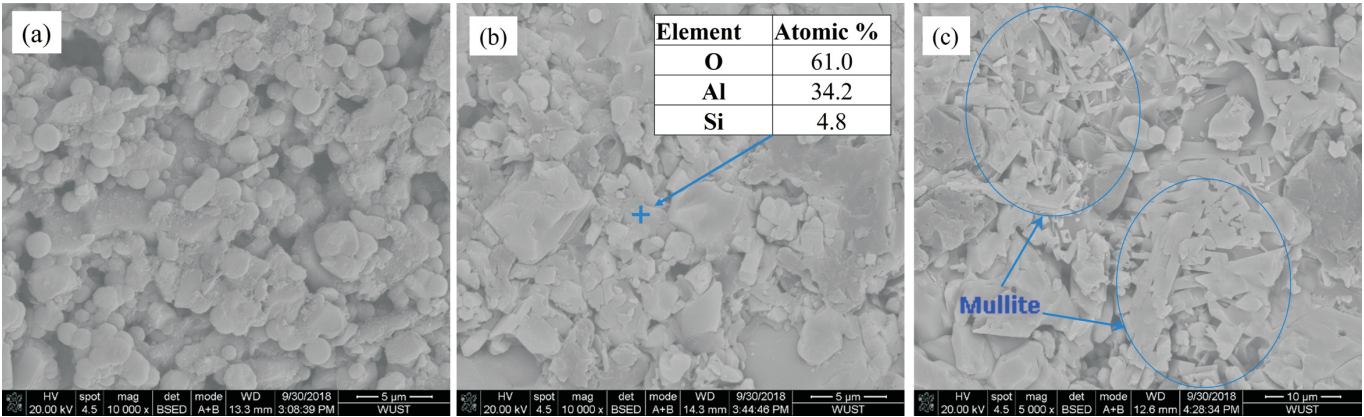


Fig. 9: SEM micrographs of etched polished surfaces of NCC-SZ specimens fired at different temperatures. (a) 815 °C, (b) 1 200 °C, and (c) 1 400 °C.

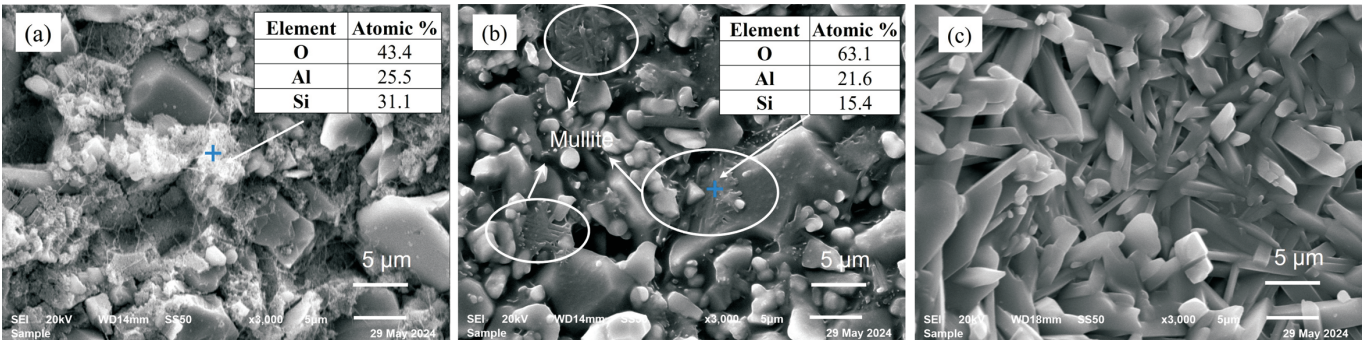


Fig. 10: SEM micrographs of etched polished surfaces of NCC-STP specimens fired at different temperatures. (a) 815 °C, (b) 1 200 °C, and (c) 1 400 °C.

The significant differences in the microstructure of NCC-STP compared to NCC-SZ demonstrated that NCC-STP began sintering with the formation of transient liquid at a low temperature of 815 °C. At this temperature, whisker phases formed as precursors to mullite formation. The subsequent formation of mullite at 1200 °C contributes to the improved hot properties and abrasion resistance of NCC-STP. This early transient liquid formation is crucial as it enhances sintering and initiates mullite formation, leading to superior mechanical and thermal properties.

IV. Conclusions

Based on the detailed results and discussions presented in this study, it can be concluded that the innovative cement-free binder systems, particularly NCC-ST and NCC-STP, have demonstrated significant performance enhancements in key properties of refractory castables compared to traditional LCC and reference NCC-SZ samples. These enhancements include improved flowability, mechanical strength, hot modulus of rupture, abrasion resistance, and refractoriness under load.

The NCC specimens exhibited superior self-flow and vibration-flow properties, highlighting their excellent workability. Additionally, NCC-ST and NCC-STP showed significantly higher mechanical strength and hot properties at intermediate temperatures, surpassing the performance of NCC-SZ and being comparable to LCC. The novel binder systems in NCC-ST and NCC-STP facilitated enhanced sintering and mullite bonding formation, leading to improved mechanical properties.

Moreover, the hot modulus of rupture (HMOR) results indicated that NCC-ST and NCC-STP outperformed NCC-SZ, particularly at intermediate temperatures. The abrasion resistance tests further reinforced the superiority of NCC-ST and NCC-STP in resisting wear and tear under high temperatures, with NCC-STP exhibiting the best performance.

The Refractoriness Under Load (RUL) tests provided valuable insights into the behavior of the refractory materials under varying conditions, emphasizing the role of binder systems in influencing thermal stability, sintering, and phase transitions. The NCC specimens with innovative binders exhibited superior mullite formation and thermal performance compared to LCC, showcasing their potential for diverse industrial applications.

Overall, this study significantly advances the understanding of how binder types influence the properties of refractory castables and emphasizes the potential of innovative cement-free binder systems in improving the performance of these materials across a range of temperatures. The results serve as a foundation for further investigations into optimizing binder compositions and their impact on the mechanical and thermal characteristics of refractory castables. These findings offer valuable insights into the development of innovative NCC castables for intermediate temperature applications in various industrial sectors, including but not limited to aluminum, petrochemicals, and power plants. Future research will focus on exploring the correlation between binder systems and their high-temperature performance, as well as the kinetics of mullite formation during the sintering process.

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