Towards Improved Refractory Lining Performances: A Novel Cement Free Binder System as Solution for Tilting Runners

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ABSTRACT

A novel cement free Al_2O_3-SiC-C castable has been developed; the new bonding system, so-called ZEO technology, is inspired by zeolite microstructure. The new cement free black castable reveals a high and rapid development of green mechanical strength during curing, providing installers time saving and ensuring safe demolding and mechanical operations. As for hot physical properties, the non-cement castable shows high hot modulus of rupture, resulting in a better resistance to the iron stream impact limiting, therefore, the risk of breakthrough.

The new binding system enables Al_2O_3-SiC-C castables to offer better performance than ultra-low cement castables or sol/gel bonded castables regarding commissioning and running time when blast furnace operations become more severe and/or when wear lining sets stringent requirements on refractories, especially in the iron stream impact zones.

INTRODUCTION

Iron tilting runner, one of the facilities of iron making, is employed on the casthouse floor to transfer the molten iron tapped from the blast furnace to torpedo ladles (Fig. 1). In recent years, the performance of blast furnace has gradationally increased, resulting in high productivity and high iron temperatures. Thus, high expectations are placed on the refractory linings of tilting runners to maintain sufficient durability even under stringent operational conditions. The severe wear at the impact zone results in downtime for repairs or new linings [1].

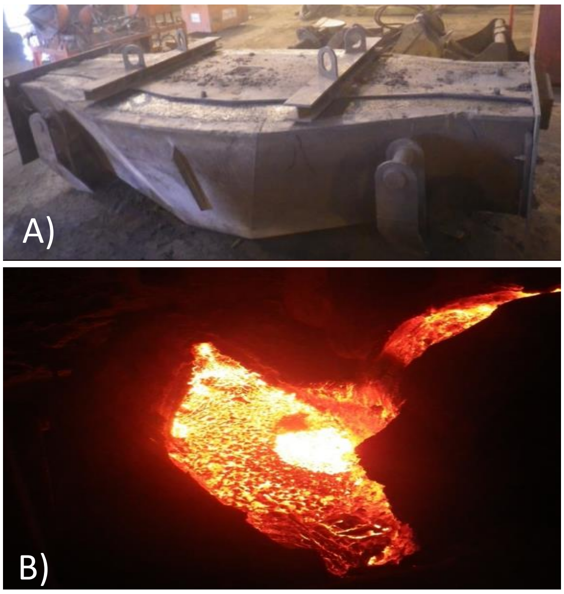

Fig. 1 *Iron tilting runner: A) Installation – B) In operation*

Even though, used universally as linings for runner and tilting runners in iron industry, cement black castables suffer from several drawbacks especially during the drying step and show some extent for harsh conditions, high temperatures, resulting in lower performance of the working lining.

Over the past years, investigations on sol/gel castables have been carried out aiming to reduce the drying times, cracking and explosion and improve hot properties such as hot modulus of rupture. Nevertheless, nanostructured bonded materials show inherent drawbacks including the poor green mechanical strength and the sensitiveness due to ambient conditions and/or ageing [2].

In order to overcome these problems and suit combinations of all requirements, a novel cement free binding system, inspired and reproducing fundamental features of zeolites, has been developed.

First and foremost, the paper tackles the key properties of zeolites structures. The effect of this novel free cement bonding system on rheological properties, setting and green strength development kinetic as well as hot properties of vibratable Al_2O_3-SiC-C castable in comparison with cement based castable and sol/gel castable will be addressed over a second phase.

ZEOLITES

Zeolite is a family of microporous, aluminosilicate minerals, either natural or synthetic [3] [4] [5]. They are crystalline, hydrated alumino-silicate of alkaline elements. Zeolites have basically three different structural variations. There are chain-like structures whose minerals form acicular or needle-like prismatic crystals, i.e. natrolite. It can also be sheet-like structures where the crystals are flattened platy or tabular with usually good basal cleavages, i.e. heulandite, or framework structures where the crystals are more equant in dimensions, i.e. Chabazite. Zeolites are framework silicates consisting of interlocking tetrahedrons of SiO_4 and AlO_4. The alumino-silicate structure is negatively charged and attracts the positive cations that reside within. Zeolites have large vacant spaces or cages in their structures that allow space for large cations such as sodium, potassium and calcium. The spaces are interconnected and form long wide channels of varying sizes depending on the mineral. This infinitely extending structure leads to the classification of zeolites as inorganic polymers. Besides, de-hydration occurs without modification of micro structure, destruction of the network or modification of the alumino-silicate skeleton.

Based on that statement, a novel cement free bonding system, inspired and reproducing fundamental features of zeolites, has been developed to meet installers and end users' expectations. A Al_2O_3-SiC-C vibrated refractory castable dedicated to tilting runners was designed from this new binder.

FORMULATIONS

Three Al_2O_3-SiC-C vibrated refractory castables, characterized by similar grain size distribution and composition at the exception of their bonding system: Ultra Low Cement Castable (ULCC), ZEO-technology based castable (ZEO) and Sol Gel bonded castable (SG) have been prepared according table 1.

Tab. 1 *Compositions of alumina based castables*

Raw Materials (%)		ULCC	ZEO	SG
Skeleton	BFA 3-10mm	34	34	34
	BFA 0-3mm	46	46	46
	Silicon carbide	5	5	5
Matrix	Calcined alumina	11,5	10	11,5
	Carbon	Yes	Yes	Yes
	Drying additive	Al	Al	/
	Cement 70% Al2O3	1,5	/	/
	Additive Z	/	3	/
	Colloidal Silica (40w. % of solids)	/	/	5,9
	Dispersant	0,05	0,05	0,05
Properties				
Water content (w.%)		3,6	3,6	3,6

Materials were mixed with identical amount of water (quantity of colloidal silica being adjusted to bring same amount of water) in identical conditions. All mixes have been mixed and casted according identical procedure. Castables are dry homogenized for 5 min and mixed with water or colloidal silica in a paddle mixer for 5 min, then cast under vibration into test bar molds. The rheological behavior is evaluated with a flow table apparatus just after mixing.

METHODS

Cold Crushing Strength

Aiming to evaluate the Cold Crushing Strength (CCS), which represents the ability of a product to resist failure under compressive load at room temperature, samples of the designed castables where cured 24 hours at 20°C in a 100% moisture atmosphere, followed by a drying step at 110°C for 24 hours before firing at dedicated temperature. The green strength which refers to cold crushing strength developed during the curing stage is measured after 24 hours curing at 20°C.

Hot Modulus of Rupture

Among the existing high temperature properties, the hot modulus of rupture (HMOR) provides the flexural strength at elevated temperatures which is a true indicator of the suitability and performance of a refractory (Fig 1). HMOR refers to the maximum stress of a rectangular test piece of specific dimension which can withstand maximum load until it breaks at high temperature. Aiming at assessing the HMOR of the designed refractories castables, rectangular testing pieces (4x4x16 cm) are fired at 1450°C under reducing conditions for 5 hours. Samples are embedded in a mix of metallurgical coke / carbon black in a silicon carbide sealed box. HMOR are measured at 1450°C in air by the three-point bending method. A quick heating rate (8°C/min) and a short dwell time (30 min) were chosen for limiting carbon oxidation.

Refractoriness Under load

In order to assess refractoriness under load (RUL) of the designed refractories, cylinders Ø50 mm x h50 mm with central hole of Ø12 mm were prepared by drilling and grinding of samples 230x64x54mm. The determination of the deformation of dense shaped refractory products, under conditions of progressively rising temperature 300°C/hr, was done according to the standard ISO 1893. The tests have been carried out under reducing conditions, inert gas flow of 5% H_2 and 95% Ar, up to a maximum temperature of 1 700 °C in NETZCH furnace. The RUL test runs with a load of 0,1 N/mm² on a pre-fired sample at 1500°C for 5hrs.

RESULTS & DISCUSSION

Flowability and Green Strength

Vibratable flows of the three designed castables are compared in table 2. The non-cement castable (ZEO) shows higher flowability than others, at water content of 3.6 w.%. ZEO castable as well as ULCC can withstand safe mechanical operations since they develop a high green strength.

Tab. 2 *Flowability and Green strength*

	ULCC	ZEO	SG
Vibratable flow (%)	135	143	132
Green Strength (MPa)	12	14	4

Following mechanical strength development versus time allows green properties comparison between ZEO and SOL-GEL castables (Fig 2). Two parameters can be identified: the kinetic of green strength development and the level of green strength. Results are summarized in table 2 and figure 2. It is generally accepted by state of the art that a minimum 5 MPa green strength after 24 hours allows safe demolding. Below 5 MPa, mold has to be carefully removed.

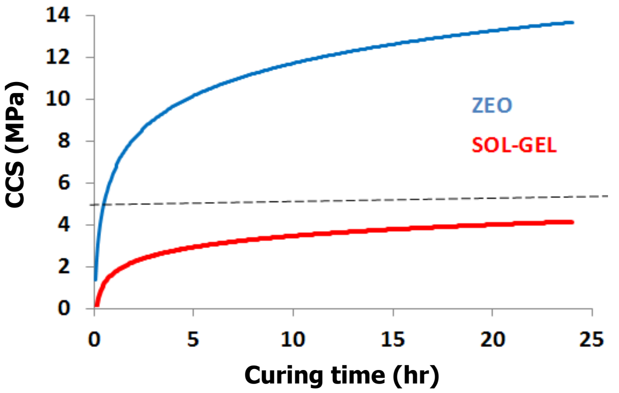

Fig. 2 *Kinetic of green Strength: ZEO castable versus SG castable.*

Kinetic comparison of green strength development shows that ZEO based castables presents rapid development of green strength higher than 5 MPa, allowing early and safer demolding compared to Sol-Gel material.

The regular arrangement of the ZEO tri-dimensional crystalline structure leads to a strong bonding strength, ensuring a high level of strength for ZEO green body. ZEO microstructure is characterized by the presence of mono-sized cavities highly interconnected together. The fact that formation of zeolithic microstructure results from infinitely extending tri-dimensional micro-structure, resulting from repetition of an identical constitutive pattern (i.e. crystalline structure), provide to the present invention a high strength bond, ensuring a high level of strength for the refractory green body. This is particularly different from other known refractory compositions such as the ones based on formation of hydrous gels that form amorphous structure (gels) exhibiting resultantly low mechanical strength, respectively low green strength refractory green body.

Hot Modulus of Rupture

Results regarding the HMOR of the designed castables are given in figure 3. From laboratory tests, HMOR is three times higher for ZEO and SG castables than for ultra-low cement castables. ZEO microstructure is characterized by low cation ratio in the formulation. Composition of ZEO matrix lies mainly in the A_2O_3-SiO_2 binary system and amount of liquid phase which forms at high temperature becomes significantly low (Fig. 4), improving ZEO refractoriness expressed by a high hot modulus of rupture. Nonetheless, low melting-temperature phases may be formed in cement containing compositions, which indeed affect the thermo-mechanical performance of CAC castables.

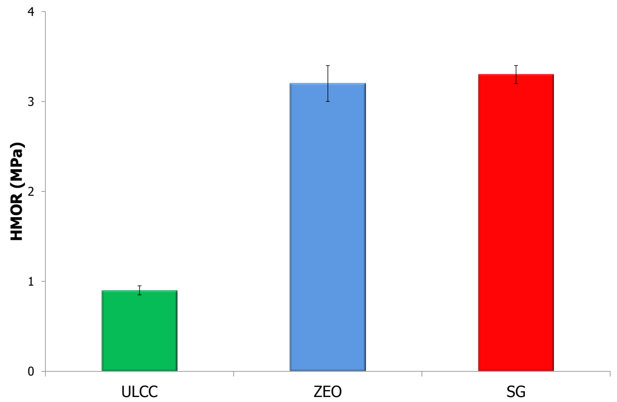

Fig. 3 *HMOR at 1450°C of ULCC, ZEO and SG castables. Samples were pre-fired at 1450°C under reducing atmosphere.*

Consequently, HMOR of Al_2O_3-SiC-C castable based on the novel cement free bonding technology becomes higher than for its regular ultra-low cement version, providing a better resistance to erosion and wear when lining sets stringent requirements, limiting therefore the risk of breakthrough.

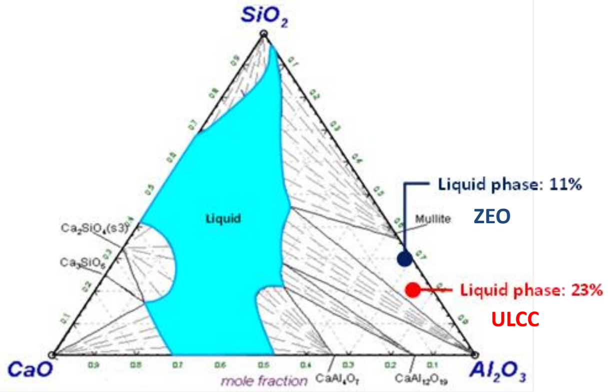

Fig. 4 *Theoretical liquid amount generated at 1600°C in Al_2O_3-SiC-C matrix of ZEO technology (blue) and ULCC (red) matrix.*

Refractoriness Under Load

Results regarding the refractoriness under load of the designed castables are given in table 3 and figure 5. In addition to the characteristic temperature length curve of the sample tested, two points on the curve are of special interest. Dmax is the maximum expansion of the specimen in percent of initial length. T 0.1 is the temperature of which the specimen shows a deformation of 0.1% calculated on the initial length in re1ation to the point of max expansion.

Tab. 3 *RUL measurements for ULCC, ZEO and SG castables*

	Dmax (%)	T 0,1 (°C)
ULCC	0,80	1553
ZEO	0,98	1601
SG	1,03	1674

Maximum dilatation and temperature at maximum dilatation are higher for the non-cement castables (ZEO and SG). From results obtained after a prefiring at 1500°C, it appears that the resistance to deformation of ZEO and SG refractory castables, when heated at high temperature and load, is higher than ULC castables. The absence of cement dramatically reduces the amount of liquid phase which forms at high temperature in the matrix of ZEO castables, compared to ULCC. This improves the maximum service temperature of the monolithic lining and its load bearing ability. RUL results confirm the higher refractoriness of both ZEO and SG castables.

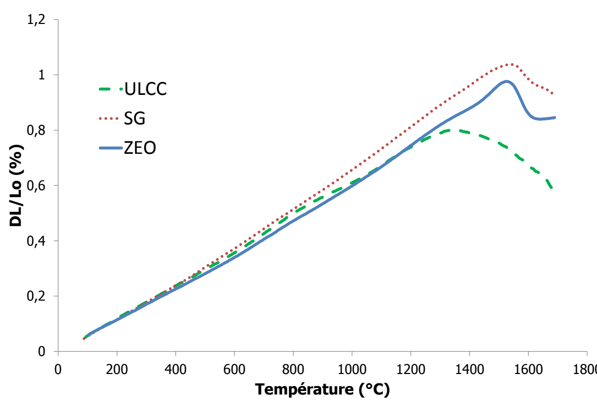

Fig. 5 *Refractoriness Under Load measurements of ULCC, ZEO and SG castables. Samples were pre-fired at 1500°C under neutral atmosphere for 5h, test occur under inert gas flow and the applied compressive load was 0.1N/mm².*

As the formation of zeolitic microstructure can be achieved with low ratio of cations for bridging $(Si,Al)O_4$ tetrahedron, present invention consists in refractory composition essentially free of alkali hearth metal oxides such as MgO, or BaO, essentially free of alkali metal oxide such as K_2O or Na_2O, and contains very low level of lime (CaO < 0.2%). Such composition, essentially of the binary system (Al_2O_3-SiO_2) enables to reach very high refractoriness as expressed by refractoriness under load or by hot modulus of rupture.

CONCLUSION

The impact area of tilting runners is often critical and limits strongly the campaign length. The production circulation and consequently the productivity can be affected, especially when the tilter has to be stopped before the main iron runner. Aiming to ensure a proper demolding and to mitigate the speed of wear in the impact zone of tilting runners, leading to a homogeneous wear profile within the tilter after operation, an Al_2O_3-SiC-C castable based on the novel cement free bonding technology has been developed. The designed material based castable presents rapid development of green strength higher than 14 MPa, allowing early and safer demolding compared to Sol-Gel material. Furthermore, ZEO castable develop a high HMOR and refractoriness since it does not generate low melting-temperature phases associated with cement bonded materials responsible for early liquid formation. This improves the maximum service temperature of the monolithic lining and its load bearing ability. In comparison of ULCC and SG castable, ZEO bonded castable combines proper installation, high safety and high performance of the working lining.

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