

# A Novel Cement Free Bonding Concept for Advanced Refractory Castables

Pierre MEUNIER, Jérôme SOUDIER and Romain TECHER.  
CALDERYS, Sezanne, France

## ABSTRACT

A novel cement free bonding technology inspired by zeolites, so called ZEO technology, has been designed to enable alumina based castables to exhibit installation and service properties that outperform state of the art technologies, such as Ultra Low Cement or Colloidal Silica bonded castables. Particularly, this new generation of castables differentiate from today's technologies by: (i) Installer benefices oriented properties with very short mixing time, outstanding long pot life without deterioration of flowability, robust, fast & adaptable to job site conditions setting behavior followed by early high strength development and (ii) Guaranteed high performances with high refractoriness for end user.

## INTRODUCTION

Over the last decades, with an accelerating trend over the past years, intensive research has been carried out, aiming at developing alternative bonding systems to Calcium Aluminate Cements (CAC) for refractory castables, respectively aiming at buffering CAC inherent drawbacks.

Even if used successfully and widely as primary bonding constituent for refractory castables, CAC intrinsic chemistry and hydration mechanism result in limitations when combination of ultra-tailored properties such as high refractoriness, robust and conditions independent placement behaviour, long workability followed by rapid development of high green strength level and safe drying are needed for refractory castables.

Academics, raw materials suppliers and refractory makers have thus designed alternative bonds, mainly based on Sol-Gel concepts [1] or on hydrated gels formation such as Magnesia-Silica or Alumina-Magnesia hydrated gels. On a parallel way, tremendous efforts have been done for developing additives to CAC, respectively for modifying CAC, in order to extend its range of applications.

These attempts permit to solve some of the upper listed drawbacks efficiently, but barely permit to achieve combinations of all targeted ultra-tailored properties at the same time.

Based on that statement, a novel bonding system has been developed for permitting such a simultaneous combination of properties in refractory castables. Unlike nanostructured and geopolymer bonded materials, this new generation of castables, once mixed with water, develops a clear set leading to microstructure mimicking zeolite microstructures.

After a brief recall of key properties of zeolite structure, the present paper focusses on the effect of this novel free bonding system on rheological properties, setting and green strength development kinetic, mechanical properties, and refractoriness of vibratable alumina castables compared to state of the art bonding systems.

## ZEOLITES

Zeolites are crystalline, hydrated aluminosilicate of alkaline elements [2] [3] [4]. Structurally they are made of infinitely extending mono-dimensional (as for natrolite  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ ), bi-dimensional (such as in heulandite  $7\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot\text{CaO}\cdot 6\text{H}_2\text{O}$ ), or more commonly tri-dimensional (such as in chabazite  $4\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot\text{CaO}_6\text{H}_2$ ), networks of  $(\text{Si},\text{Al})\text{O}_4$  tetrahedra, which constitute the primary building units, that are connected by metal cations. This infinitely extending structure leads to the classification of zeolites as inorganic polymers.

The above mentioned networks are characterized by the presence of large monovalent or divalent ions such as  $\text{Na}^+$ ,  $\text{K}^+$  or

$\text{Ca}^{2+}$  distorting the organization of  $(\text{Si},\text{Al})\text{O}_4$  tetrahedra and responsible for the distribution of large interconnected voids spaces within the framework.

Zeolites, respectively zeolite structures are thus characterized by three main characteristics, an alumina silica network, the presence of large interconnected void spaces and a structure containing metal cations such as  $\text{Ca}^{2+}$ . The above main characteristics confer to zeolites and zeolitic structures particular properties such as:

(i) Formation of micro-structure, i.e. connection of  $(\text{Si},\text{Al})\text{O}_4$  tetrahedra, governed by presence and by concentration of cations; (ii) Infinitely extending tri-dimensional micro-structure, resulting from repetition of an identical constitutive pattern; (iii) Micro porosity, i.e. low intrinsic density and large void volume after de-hydration, voids being filled with water prior dehydration. Porosity (voids) is characterized by the fact it is essentially mono-sized and highly interconnected; and (iv) De-hydration without modification of micro structure, destruction of the network or modification of the aluminosilicate skeleton.

Considering this statement, a novel cement free bonding system, inspired and reproducing fundamental features of zeolites, has been developed to meet installers and end users' expectations.

## FORMULATIONS

Three tabular alumina cast vibrated refractory castables, characterized by similar grain size distribution and composition at the exception of their bonding system: Ultra Low Cement (ULCC), ZEO-technology (ZEO) and Colloidal Silica (SG) have been prepared according table 1, then mixed with identical amount of water (quantity of colloidal silica being adjusted to bring same quantity of water) in identical conditions.

**Tab. 1** Compositions of alumina based castables

Raw Materials (w.%)		ULCC	ZEO	SG
Aggregates	Tabular Alumina 3-6mm	39	39	39
	Tabular Alumina 1-3mm	10	10	10
	Tabular Alumina 0-1mm	31	31	31
Matrix	Calcined Alumina	13	13	14,4
	Microsilica	6	4,5	3
	Colloidal Silica (40w.% of solids)	/	/	6,4
	Cement 70% $\text{Al}_2\text{O}_3$	1,3	/	/
	Additive Z	/	3	/
	Dispersant	0,05	0,05	0,05
Properties				
Water content (w.%)		3,8	3,8	3,8

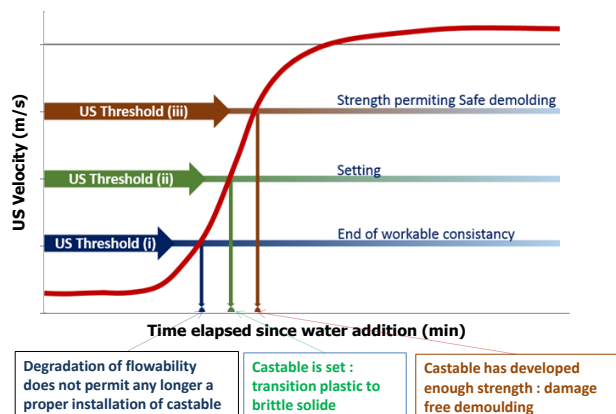
Castables are dry homogenized for 5 min and mixed with water or colloidal silica in a paddle mixer for 5 min, then cast under vibration into test bar molds ( $64\times 54\times 230\text{ mm}^3$ ). The rheological behavior is evaluated with a flow table apparatus just after mixing with the proper amount of water.

## METHODS

### Ultrasonic Velocity Measurements

Measuring Ultrasonic waves propagation speed [5], representative of consistency and stiffness of respectively fresh and hardened castable, permits to accurately identify three thresholds (Fig 1). The first one is the maximal degradation of flowability permitting placement by cast vibration - Threshold (i). The second one is the setting, transition from liquid or plastic consistency to stiff solid, - Threshold (ii). And the third

one is the green strength level enabling safe and damage free demolding - Threshold (iii).



**Fig. 1** US technic & associated castables installation properties. Ultrasonic velocity as a function of time

### Mechanical 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, and the Modulus of Rupture (MOR), which indicates the material bending strength and its suitability for use as refractory lining; samples of the designed castables were cured 48 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 48 hours curing at 20°C.

### Refractoriness Under Load

In order to assess the refractoriness under load (RUL) of the designed materials, cylinders Ø 50 mm x h 50 mm with central hole of Ø 12 mm were prepared by drilling and grinding of samples 64x54x230mm<sup>3</sup>. The determination of the deformation of dense shaped refractory products, when subjected to a constant load (0.1N/mm<sup>2</sup>), under conditions of progressively rising temperature (300°C/hr), was done according to the standard ISO 1893. The tests have been carried out up to a maximum temperature of 1 700 °C in NETZCH furnace.

## RESULTS & DISCUSSION

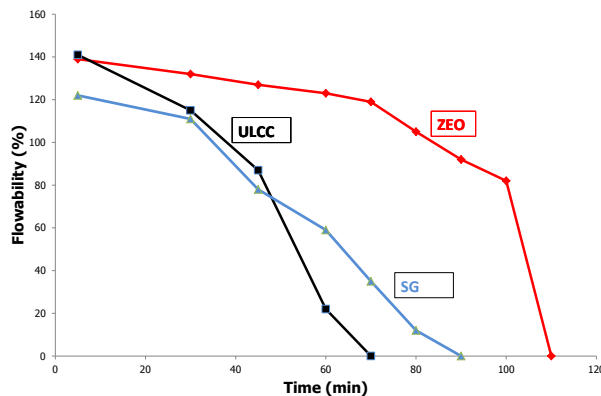
### Flow, Setting and Strength

Vibration-flow values are summarized in table 2. The non-cement castable (ZEO) shows similar flowability that the ULCC, at water content of 3.8 w.%,. On the other hand, the flowability of the silica-sol bonded castable is lower than others.

**Tab. 2** Flowability and CCS of alumina based castables

	ULCC	ZEO	SG
Flowability (%) - 3,8% water	141	139	122
Green Stength (MPa)	18	18	1
MOR (MPa)	3,0	3,2	0,1
CCS (MPa) at 110°C	60	60	65

ZEO castable shows a long pot life without deterioration of flowability (Fig. 2), providing installers with easy and versatile casting solution. It exhibits a long working time, 90 minutes to reach stiffened consistency allowing no more practical casting, without seeing its fluidity affected; Colloidal silica bonded castables and ULCC demonstrates significantly shortened pot life, assorted with continuous degradation of their flowability .



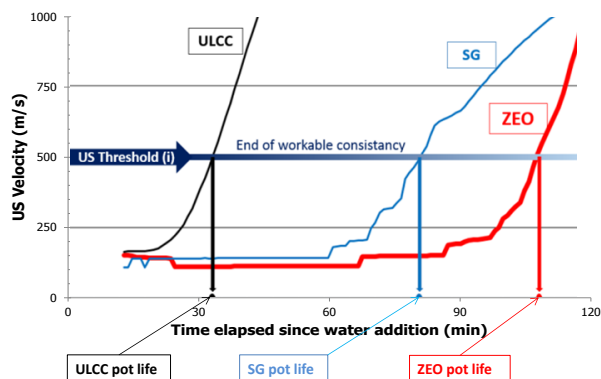
**Fig. 2** Flowability of ULCC, ZEO and SG castables.

The fact that formation of zeolitic microstructure, by connection of (Si,Al)O<sub>4</sub> tetrahedra, is happening when solubilization of calcium source has permitted to reach a given minimal concentration of Ca<sup>2+</sup> in the system, permit to have a long dormant period (i.e. no formation of new species, no creation of bond), also called “working time”: time elapsed after mixing with liquid without deterioration of flowability.

This is particularly different from other known refractory compositions such as the ones based on formation of hydrous gels, for example bonding systems based on destabilization and coagulation of silica colloids sols. In this case reaction between silica colloids by formation of hydroxyl bonds between particles (Si – O – H – O – Si) starts as soon as silica sols has been in contact with impurities disturbing its initial stabilization, i.e. decrease of flowability starts as soon as silica sol has been mixed with refractory particulate compositions.

### Set behaviour and strength

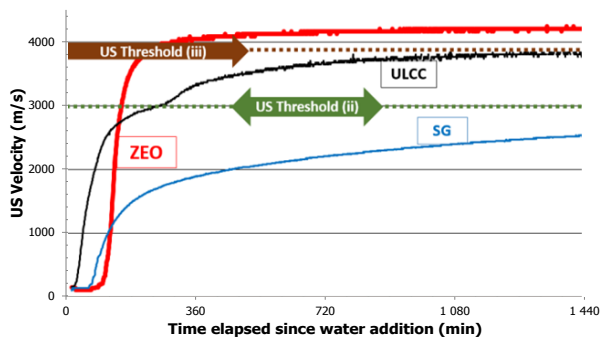
Evolutions of ultrasonic speed propagation till threshold (i), i.e. till end of their respective pot life, for ZEO, ULCC and SG are compared in figure 3. Whereas Ultra Low Cement and Colloidal Silica bonded products exhibit short pot life, respectively 35 min and 80 min, ZEO technology based castable demonstrates an outstanding long pot life (110 min), permitting easy and compatible with job site realities installation. Regarding castable consistency, when ULC & Colloidal Silica bonded castables exhibit continuous deterioration of the flowability over their short pot life, ZEO technology based castable demonstrates a constant and high flowability all over it workable period. This permits installer to place ZEO products with same easiness and same quality of vibration all over the longer available workable time.



**Fig. 3** Evolution of consistency till end of pot life of ULCC, ZEO and SG castables. Ultrasonic velocity as a function of time.

Evolutions of ultrasonic speed through thresholds (ii) and (iii), representative of setting time & duration, as well as of strength development, are illustrated in figure 4 for ZEO, ULCC and SG.

These results highlight three major differentiated behaviors of ZEO technology based castable versus benchmark. The first one is when ULCC reaches threshold (ii), that is to say “setting time”, after respectively ca. 4 hours, when Colloidal Silica bonded castable has not yet reached full set after one day, ZEO technology based castable demonstrates a significant earlier setting, 1.5 hours. Secondly, ZEO castable exhibits a very short period of time for evolving from threshold (i) to (ii), in other words it exhibits a reduced setting duration; while ULCC and colloidal silica bonded castables suffer from a significant longer setting duration. The last point is when ULCC castable reaches a mechanical strength compatible with safe and damage free demolding after 1 day (threshold (iii)) and Colloidal silica bonded castables has not yet set, ZEO technology based castable can be demolded as early as few hours after its installation. The fact that, zeolitic crystalline tri-dimensional framework undergoes de-hydration without modification of micro structure, destruction of the network or modification of the aluminosilicate skeleton, provides high mechanical strength to the green bodies of the material.



**Fig. 4** Setting behavior and strength development of ULCC, ZEO and SG castables. Ultrasonic velocity as a function of time.

### Hot properties

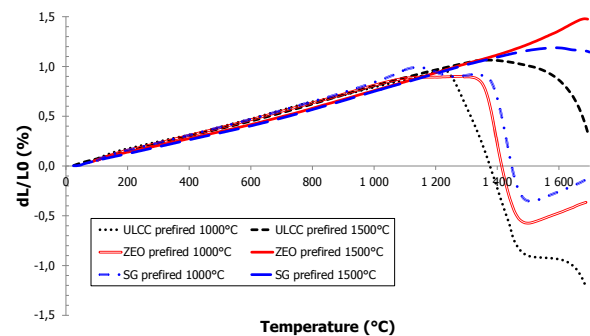
Results regarding the refractoriness under load of the designed castables are given in table 3 and figure 5. Aiming to assess the influence of the pre-firing temperature, samples were pre-fired at 1000°C and 1500°C. In addition to the characteristic temperature length curve of the sample tested, four points on the curve are of special interest.  $D_{max}$  is the maximum expansion of the specimen in percent of initial length.  $T_{0.1}$ ,  $T_{0.5}$  and  $T_1$  are the temperatures of which the specimen shows a deformation of respectively 0.1%, 0.5%, 1% calculated on the initial length in relation to the point of max expansion.  $T_{0.5}$  is considered as the start of the softening.  $T_1$  is considered as the end of the softening range.

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

	$D_{max}$ (%)	$T_{0.1}$ (°C)	$T_{0.5}$ (°C)	$T_1$ (°C)
ULCC prefired 1000°C	0,97	1256	1317	1379
ZEO prefired 1000°C	0,90	1355	1389	1422
SG prefired 1000°C	0,99	1261	1415	1449
ULCC prefired 1500°C	1,07	1545	1660	/
ZEO prefired 1500°C	1,48	>1700	/	/
SG prefired 1500°C	1,19	>1700	/	/

Materials are usually tested after pre-firing at 1000°C. Consequently the samples are totally dehydrated and the coefficient of reversible thermal expansion can be determined from the expansion between 20 and 1000°C when no thermo-plasticity takes places. Some castables are already totally stabilized after firing at 1000°C. In this case, the final softening (permanent visco-plasticity) which appears at high temperature defines the refractoriness. The materials which have a high refractoriness may transform and stabilize at a higher temperature than 1000°C. In this case, a transient visco-plasticity appears which takes place during the reorganization /

transformation at  $T > 1100^\circ\text{C}$ . Under a load of 0.1 N/mm<sup>2</sup>, castables with  $\text{CaO} \leq 0.2\%$  (ZEO and SG castables) slump by more than 1.5%, before expanding again at higher temperatures. In the case of ULCC, which contains more CaO and hence forms more liquid phase, this reexpansion is not observed.



**Fig. 5** Refractoriness Under Load measurements of ULCC, ZEO and SG castables. Samples were pre-fired at 1000°C or 1500°C for 5h and the applied compressive load was 0.1N/mm<sup>2</sup>.

For the two types of non-cement castables expansion stops at around 1100°C, instead of 1200°C for ULCC. Some transformations already take place between 1100°C and 1300°C which cannot be seen with ULCC. Transient visco-plasticity probably takes place during the structural reorganization linked to mullite formation. Castables with a high refractoriness, ULCC, ZEO or SG, are not stabilized after firing at 1000°C, unlike conventional, medium and low cement castables. So the standard procedure consisting in pre-firing the test sample at 1000°C and measuring  $T_{0.1}$ ,  $T_{0.5}$  and  $T_1$  is not suitable to determine refractoriness. Transient visco-plasticity interferes, which occurs during a reorganization / transformation of the material at  $T > 1100^\circ\text{C}$ . Prefiring should be performed at a much higher temperature (above 1300°C) to test the refractoriness of a stabilized material. However the test performed after pre-firing at 1000°C has the interest of showing the extent of the transient visco-plasticity.

From results obtained after a pre-firing at 1500°C, it appears that the resistance to deformation, when heated at high temperature and load, of ZEO and SG refractory castables is higher than ULCC 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.

### CONCLUSION

A novel bonding system, so-called ZEO technology, inspired and reproducing fundamental features of zeolites, has been developed. The evaluation of high alumina refractories castables based on the novel non cement binding system indicated that such castables led to outstanding installation properties combined with superior hot properties in comparison with sol gel castables and CAC materials. Particularly, this new generation of castables differentiates from today’s technologies; indeed ZEO bonding technology offers installation properties that outperform state of the art, long pot life without deterioration of flowability, robust, fast and adaptable to job site conditions setting behavior. Unlike Sol Gel materials, ZEO castables show early development of high mechanical strength which ensures installers a quick, safe and damage free demolding practice. RUL tests of the ZEO castables pointed out high refractoriness ( $T_{0.1} > 1700^\circ\text{C}$ ). Superior hot physical properties provide customers with increase of the working lining life. This non cement binding system is also compatible for  $\text{Al}_2\text{O}_3\text{-SiC-C}$  castables; results will be discussed in another paper.

## REFERENCES

- [1] A.P. da Luz, M.A.L. Braulio, V.C. Pandolfelli. Refractory Castable Engineering, Chapter 4. 2015, pages 217-229
- [2] A.F. Cronstedt, J.L. Schlenker, G.H. KühlKühl. *Observations and descriptions: On an unknown mineral-species called zeolites*. Proceedings from the Ninth International Zeolite Conference, 1993, pages 3-9
- [3] H. Takeda, S. Hashimoto, T. Iwata, S. Honda, Y. Iwamoto, *Fabrication of bulk materials with zeolite from coal fly ash*. J. Mater. Cycles Waste Manag. 2012, 14, 403-410.
- [4] M.D. Shannon, *Method of solution and structure of 3 novel high alumina medium pore zeolites with multi-dimensional channel systems*, Proceedings from the Ninth International Zeolite Conference, 1993, pages 389-398.
- [5] F. Simonin, C. Wöhrmeyer, C. Parr, *A new method for assessing calcium aluminates cements*, Proceedings from the 9th Biennial Worldwide Congress UNITECR, Orlando, United States, 2005.