CEMENT-FREE REFRACTORY CONCRETES AS TECHNOLOGY LEAP FOR SEVERAL INDUSTRIES AND APPLICATIONS

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ABSTRACT

A constant focus on the technical applications, and in particular on the economic saving potentials in several industries, results in numerous flexible, efficient and reliable innovations in the development of refractory concretes. As a result the share of monolithic products of the world-wide refractory market increases year by year. Cement-containing refractory concretes are considered to be standard in many industries and applications, although a major drawback of these materials is their long and complex curing and drying phase. The heating of such linings may cause higher energy costs and longer downtimes of the furnace. Thus, in linings designed with shaped and monolithic refractories the typical cement-bonded products limit the efficiency of the refractory commissioning procedure. At present, the development of preferentially two different no-cement concrete concepts, namely cement-free refractory concretes which are installed simply with water or with a highly reactive liquid binder, represents a significant technical advance. This paper presents a comparison of cement-containing refractory concretes with these novel no-cement concepts embodying an optimized microstructure. In this context, the easy and simple application, a faster drying and heating with a reduced risk of explosion damage, a shorter time for re-commissioning, veneering aspects as well as a stress-reduced performance and improved high temperature properties of these cement-free refractory concretes are accentuated. A constant focus on these multifaceted and closely interconnected demands has resulted in new refractory concrete concepts, which allow simple handling with safe installation and high performance in highly stressed plant areas of different industries in the foreground.

INTRODUCTION

Not only in the recent past the requirements for energy-saving processes has significantly increased. In the case of refractory products this has led to an increase of monolithic materials at the cost of fired brick products, as concretes are installed at the customers plant and do not need firing or heat treatment at the producers' site, Fig. 1. Furthermore, the development of sophisticated installation equipment, like wet-gunning machines or special high-tech nozzles of dry gunning equipment, provides product properties, e. g. higher strength and lower porosity, which can be even superior to pressed bricks.

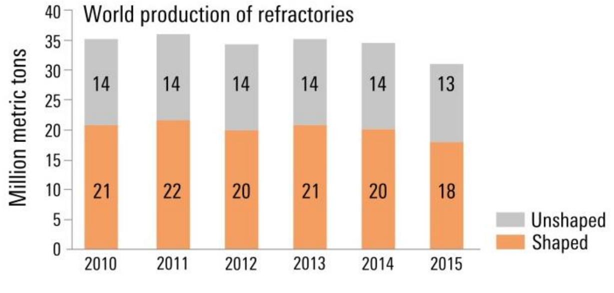

Fig. 1: Ratio of the amount of shaped and unshaped refractories according to [1]

Still, the heating-up behaviour of cement-containing concretes has been focused. This slow and controlled drying process costs not only money, but also time, as the physically and especially the chemically bonded water has to be securely driven out of the lining, otherwise explosions and damage to the lining may occur. This has led to the development of cement-free refractory concretes, which can be heated much faster than conventional concretes and even provide superior properties.

Based on the general definition, no-cement concretes (NCC) may contain up to 0.2 % CaO. Such cement-free concretes are not a new invention at all. They have been widely used for many years and have existed always beside the cement-containing concretes. Due to the trend of reducing the cement content, NCC's have taken a new boom, which is based on increased requirements on the monolithic refractories. As a result calcium aluminate-bonded systems are no longer automatically the first choice. Cement-free bonding systems may be divided into two main groups:

a) chemical, mineral, inorganic and non-hydraulic e.g. water glass, phosphates, acidic binders, chromates geopolymers, chlorides, sol-gel systems, sulphates, fries and glass etc.
b) organic e.g.: lignin sulfonate, pitches and resins

Additionally, ceramically bonded concretes should be mentioned as they are used for EAF hearth ramming mixes.

In this paper, the latest developments for the economically most important geopolymer and silica-sol-gel concretes are emphasized.

GEOPOLYMER-BONDED CONCRETES

Essential for a dry one-component cement-free geopolymer concrete activated by alkalis (2, 3) is a favourable ratio between physically and chemically bonded water and an optimized microstructure with high permeability to achieve a low water vapour pressure during heating to permit easy drying, (4). Low cement concrete (LCC) binding phases show a very dense and compact microstructure with mainly micropores < 0.1 µm and large macropores, Fig. 2, resulting in low gas permeability.

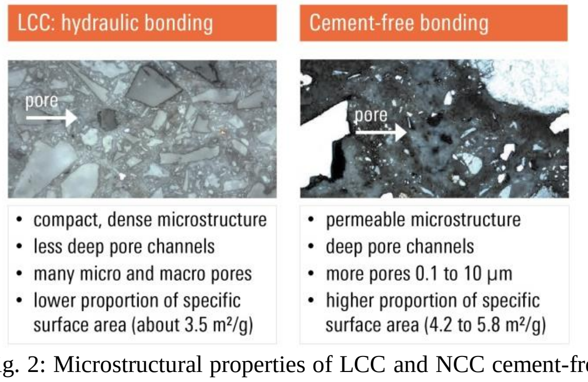

Fig. 2: Microstructural properties of LCC and NCC cement-free bonding

Contrarily, dry one-component cement-free concretes exhibit a more permeable matrix structure. The finer and deeper structure with pores between 0.1 and 10 µm increases the specific surface area to enable the water vapour to get faster out of the lining and prevents spalling at temperatures above 150 °C. This is ensured by the higher permeability (RILEM method), pore size distribution (mercury pressure porosimetry), and the amount of chemically bonded water (LECO analysis), which are superior for the cement-free concretes compared to cement-containing ones, Fig. 3.

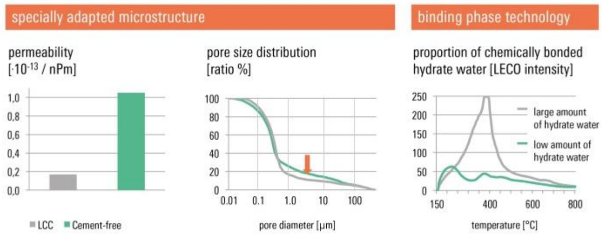

Fig. 3: Structural properties of cement-free geopolymer bonded refractory concrete for fast and safe drying compared to an LCC

Noticeably, this higher permeability does not affect the alkali resistance, which shows the same good results as cement-containing concretes.

A cement-free system exhibits a far more favourable ratio for the water evaporation than a cement-containing one, Fig. 4.

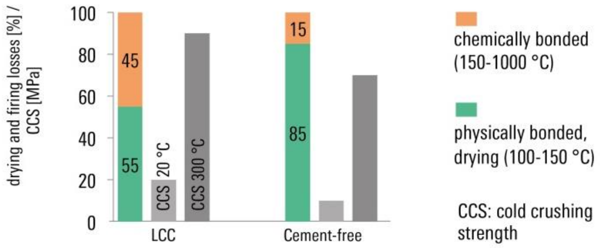

Fig. 4: Comparison of the proportions of physically and chemically bonded water as well as green and dry strengths of LCC and one-component NCCs

At least 85% of water in cement-free systems is physically bonded and can be evaporated at temperatures < 150 °C, only < 15% is chemically bonded and provides less water vapour with reduced steam pressure at critical temperatures > 150 °C. Thus, 24 h of setting recommended for cement-containing concretes is not essential for cement-free one-component concrete linings, Fig. 5. On further heating, the permeable microstructure permits the drying period to be cut by half compared to cement-containing concretes. The heating rate can be up to 50 K/h.

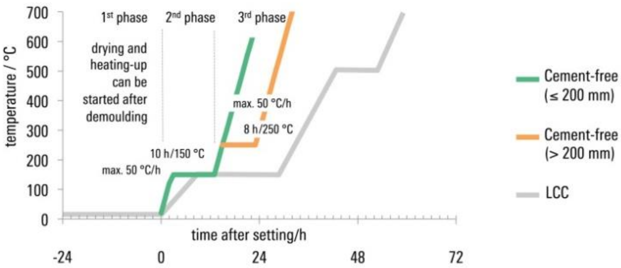

Fig. 5: Recommended drying of cement-free refractory concretes

Especially with short-term downtimes, the shortened drying and heat-up phases of cement-free refractory concretes permit a faster return to normal production.

This cement-free technology also offers outstanding thermomechanical properties – at temperatures up to 1600 °C it shows an excellent strength combined with high elasticity (Fig. 6).

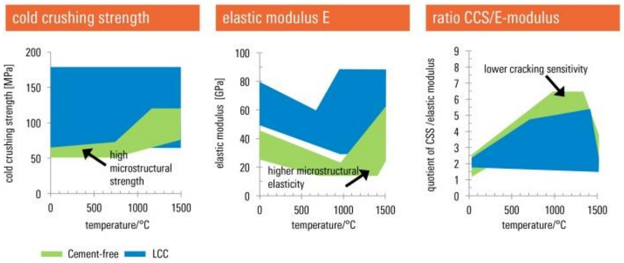

Fig. 6: Outstanding thermomechanical properties of cement-free geopolymer bonded concretes

Already below 800 °C, low-cement concretes exhibit very high strengths. After drying, one-component cement-free concretes have high strengths and thereby an increased resistance to cracking. With all binding phase concepts, the strength values increase significantly at temperatures exceeding 1000 °C.

In the high temperature range, cement-containing products in particular exhibit a high modulus of elasticity and high brittleness characterized by a very high cold crushing strength, Fig. 6. Characteristically, cement-free products have a lower Young's modulus and a high microstructural elasticity at high temperatures.

This results in a superior performance in areas subjected to mechanical stresses, proven by installations in the nose ring and the cooler inlet chute as shown in Fig. 7. A cement-free bauxite concrete after 4 months showed no thermomechanical or thermochemical wear in the area of the outlet segments.

Fig. 8 shows linings of a burner pipe and a kiln hood roof without premature wear as it was formerly observed with cement-containing concretes.

Fig. 7: Cement-free geopolymer bonded bauxite concrete in highly loaded areas of cement plants

Fig. 8: Cement-free andalusite geopolymer bonded concrete in highly loaded areas of cement plants

SILICA-SOL-GEL-BONDED CONCRETES

Sol-gel-bonded refractory concretes are basically two-component materials consisting of a dry component and a liquid binder (silica-sol). The dry component is cement-free and contains all additives required for the processing and the setting. The liquid binder is a stable solution of SiO_2 particles in water with a particle size diameter between 5-75 nm. Solid concentration of the silica-sol is between 20-50 wt%, and in combination with the specific surface area of this liquid binder (200-500 m^2/gr), there is a large reaction potential to corresponding components of the dry component. After mixing of the liquid binder with the dry component, the setting process can be initiated by polymerization. The liquid binder forms a three-dimensional network by conversion from the sol to the gel state. At ambient temperature this binder creates a cold crushing strength (CCS) (20 °C) of 5-10 MPa. By rising the temperature a sol-gel-bonded concrete achives a CCS of 35 MPa at 110 °C; at higher temperatures (> 800 °C), the highly reactive SiO_2 component of the liquid binder and the reactive alumina of the dry component cause an additional formation of mullite, which reinforces the binding matrix and leads to a significantly higher strength (> 100 MPa). One big advantage of cement-free, sol-gel-bonded concretes is the shortening of necessary drying and heating up times. Based on the finer pore structure and the increased specific surface area, the water vapour gets faster out of the lining. Higher permeability, finer structure and distribution of the pores, in combination with a small amount of chemically bonded water, result in significantly faster commissioning of repaired furnace assemblies. Additional to this central and important item, there are further characteristic quality signs of sol-gel-bonded concretes.

1. Adhesion to used refractory surface

Repairs with cement-bonded concretes on top of worn out refractory surfaces are fundamentally problematic since this bonding system generates only a small interlocking with the substrate. Such repaired zones can be separated again at the contact surface after a short time. Due to its high reactivity, the silica-sol binder reacts not only with the concrete components, but also with the worn refractory surface, and causes an equally strong bond in the contact zone, as shown by laboratory tests, Fig. 9.

Fig. 9: Sample preparation for the evaluation of the bonding strengths in the contact zone: MCC (bauxite) sol-gel (WFA) concrete after pre-firing at 1000 °C/5 h. Separation by MOR of 21 MPa through concrete structure, no separation in the contact zone.

2. Installation on hot refractory surface

Hot repairs with cement-based concretes are almost impossible, since the hydrate phases form a dense structure which is immediately repelled by the escaping water vapour. Sol-gel-bonded refractory concretes have a much higher permeability and a significantly lower proportion of chemically bonded water. In contrast to hydraulically bonded concrete, this characteristic leads to an adherent, dense concrete structure on hot surfaces.

3. Concrete installation at hot ambient temperature (> 30 °C)

Installation of cement-bonded shotcrete material at temperature of > 30 °C is to be regarded as extremely problematic, as cement bonding at high ambient temperatures shows high reactivity and extremely short processing times. Especially with shotcrete installations, this negative feature can lead to considerable installation problems. Tests in a climate chamber by temperatures up to 50 °C with two different silica-sol binder shows, that up to a mixture temperature of 50 °C the mixed concrete can be held in nearly unchanged consistency for several hours, Fig. 10.

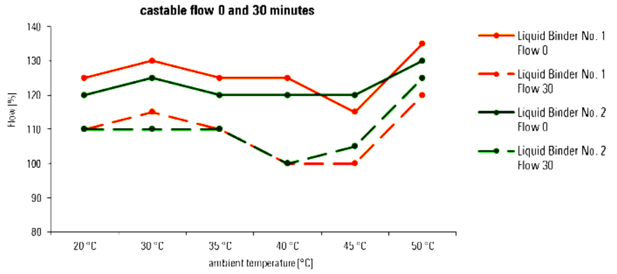

Fig. 10: Concrete consistency in accordance with BS EN ISO 1927-4:2012 for two different silica-sol binders at different temperatures after 0 and 30 min storage time.

4. Hot modules of rupture (HMOR): LCC/sol-gel bonding

In general, thermal strength of sol-gel-based materials is significantly higher than of cement-bonded concretes, Fig. 11.

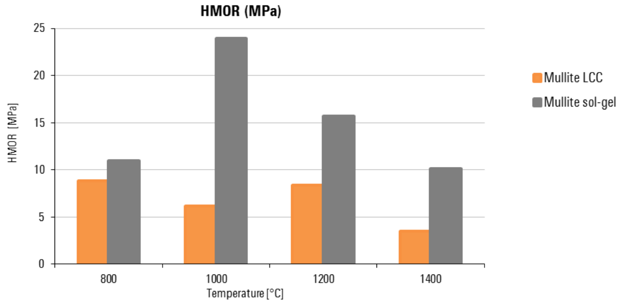

Fig. 11: HMOR of sintered mullite-based concrete (LCC vs. sol-gel)

Mineralogical and microscopic investigations of the samples showed, in direct comparison, the increased formation of mullite for sol-gel-bonded concretes, which results in a reinforcement of the microstructure and thus a higher resistance to thermomechanical loading is achieved.

5. Thermomechanical resistance and maximum service temperature

According to the standard, LCC concretes have a CaO content of up to 2.5 wt%. Thus, above 1000 °C., low-melting mineral compounds will be formed (anorthite gehlenite), which limits the application temperature. Sol-gel-bonded concretes are cement-free and located in the system Al_2O_3-SiO_2, which leads to a significantly higher service temperature, Fig. 12.

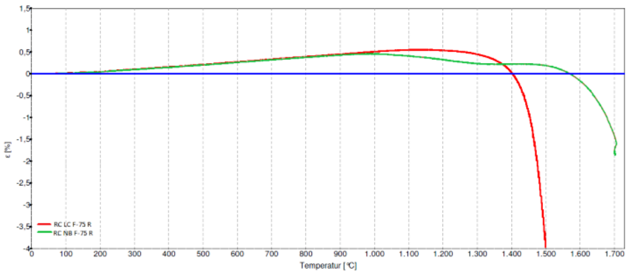

Fig. 12: Thermomechanical resistance (RUL) after pre-firing at 1000°C/5h and a load of 0,2 MPa (red: LCC, green: sol gel)

6. Resistance to acids of sol-gel-bonded refractory concrete

Hydraulic bonding systems are attacked by sulfuric acid due to their CaO component. The binding system and thus the entire concrete structure are thereby completely destroyed. SiO_2-based, CaO-free binding systems, on the other hand, have no reaction potential to acidic media and can therefore be classified as acid-resistant. Fig. 13 shows the attack of 70% H_3SO_4 to LCC and sol-gel binding systems at 20 °C/24 h (raw material base: fused silica).

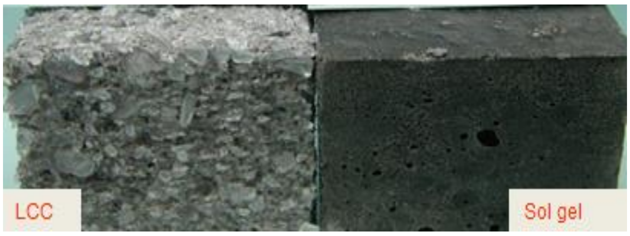

Fig. 13: Resistance to acids of LCC/sol-gel bonding

Fig. 14 shows a comparison of the acid solubility according to DIN EN 993-16 as a function of the binding system and the raw material base. Sol-gel-bonded refractory concretes based on fused silica, fireclay and SiC were compared to a hydraulically bonded concrete based on fireclay. Sol-gel-bonded concretes show significantly more favourable values, regardless of the raw material base used, as well as the pre-treatment temperature.

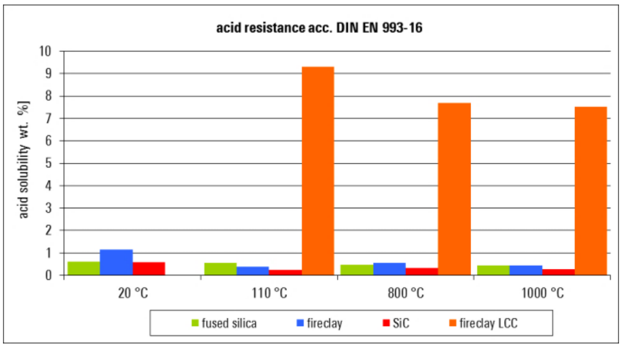

Fig. 13: Comparison raw material base, binding system, pre-firing temperature

7. Melting and treatment of Al-Alloy

Due to the low treatment temperatures in aluminium melting furnaces, cement-bonded linings show very long drainage periods due to their high proportion of chemically bonded water. This can lead to hydrogen contamination of the first aluminium melts. Then the first production must be rejected due to H_2-contamination.

Favourably, sol-gel-bonded refractory concretes have no hydrogen contamination, because the water is dried out completely at 150 °C.

CONCLUSION

In technical and economic terms, the latest developments of the cement-free one-component and sol-gel-concepts show that more than ever before, today's refractory concretes have become 'all-rounder products'.

The described cement-free technologies can be applied easily and simply with all typical application procedures, whereby economic advantages are offered in particular by the dry or wet gunning installation methods.

Moreover, the specifically designed concept of cement-free binding phases permit fast drying and heating-up as well as stress-reduced performance.

Constant focussing on these multifaceted and closely intermeshed demands resulted in a new refractory concrete concept, which places simple handling, safe installation, and high performance in highly stressed steel and cement plant areas in the foreground.

Until the invention of the sol-gel bonding and the significant improvement of the geopolymer system, NCC's played a minor role in the refractories industry. On the one hand cement-containing concretes such as LCC or ULCC provided superior properties for many applications. On the other hand many of the NCC's revealed significant drawbacks that excluded them from many applications. (restricted use of liquid phosphoric acids (critical work safety), limited hot and cold bending strength of sulphates and silicate bonds). Nevertheless, many NCC's are the given standard for several applications. Especially for bonding basic raw materials such as magnesia they provide determinant advantages. As a result their main application is the area of magnesia based lining and repairing (hot and cold).

Table 1 provides a comparison of some widely used cement-free bonding systems. The focus has been set on the differences to the cement bonding whereas their properties were added for comparison. Green colour means a general suitability and good or very good properties. The yellow sections stand for a limited practicability/workability whereas red colours indicate weaknesses of the bonding system that may restrict their applications. The installation and performance properties of the cement-free castables are generally more than competitive and allow a successful performance in numerous industries. The well-established installation behaviour for all installation methods, the possibility of a fast heating-up and the outstanding thermomechanical properties resulting in a stress reduction in the lining offer a superior performance not only limited to the steel, cement, and aluminium industry.

Table 1: Comparison of the properties of different cement-free bonding systems

	type of bonding				
parameter	cement	phosphatic	silicatic	geopolymer	sol-gel
shelf life	yellow	green	red	yellow	green
processing/installation	green	yellow	green	green	green
handling/work safety	green	yellow	yellow	green	green
drying/heating-up	yellow	yellow	green	green	green
general setting reliability	green	yellow	yellow	yellow	green
general corrosion	yellow	green	red	green	green
acid resistance	red	green	green	green	green
installation at high ambient temp.	yellow	red	yellow	yellow	green
installation at low ambient temp.	yellow	yellow	red	yellow	yellow
adhesion to ground	yellow	green	green	green	green
suitability for hot-repair	yellow	green	green	yellow	green
max. application temperature	green	red	red	green	green
strength before usage	green	green	green	green	yellow
hot bending strength	yellow	green	red	green	green
suitability for basic raw materials	red	green	green	green	red
suitability for neutral raw materials	green	green	green	green	green
suitability for acidic raw materials	green	yellow	green	green	green

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