HYBRID – INNOVATIVE BONDING TECHNOLOGY FOR REFRACTORY CONCRETE

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ABSTRACT

The commonly used bonding systems for monolithic refractory castables have several disadvantages. There is no system, which combines high strength development over the entire temperature range, fast heating up properties and sufficient high-temperature durability. This investigation compares the new Hybrid bonding system to the cement and silica sol bonding. Even at room temperature there is a significant strength increase in comparison to silica sol bonding. The uncritical heating up properties stays unaffected. All benefits of the Hybrid technology are particularly evident in practice for example in areas with high mechanical stress already at low temperatures, to produce pre-shaped components or to reduce downtimes and emissions with fast heating rates. In times with high requirements for reducing carbon emissions, Hybrid technology offers great possibilities for energy saving in industrial applications.

INTRODUCTION

The commonly and widely used binder is calcium aluminate cement (CAC) [1]. It´s main phases are calcium aluminate (CA) and calcium dialuminate (CA_2), which are solving in contact with water and after a characteristic period, hydrate phases are formed by exothermic reaction [2]. The hydrates are leading to high strength, directly after setting and at temperatures below 800 °C. Another advantage is the good adjustable setting behaviour [3]. A drawback of this system is the chemically bonding of water in hydrate phases. The point of dewatering takes place up to temperatures above 500 °C [4]. This can effectuate a tear off of the capillary channels, which are required to transport the water vapor out of the lining. In combination with the rising steam pressure, the risk of cracks or explosive spalling is increased significantly. This results in at least extremely sensitive heating rates.

An alternative is the cement free silica sol bonding, which is state-of-the-art already. A silica sol, which includes colloidal SiO_2-particles, is steering the setting process. The hydroxyl groups (SiOH) on the particle surface are reacting and leading to the formation of siloxane bonds (-Si-O-Si-). These bonds are linked to a three-dimensional network [4]. The formation of this gel and the dry out leads to a strength development and a formation of fine pores (gel pore < 0.03 µm). Advantage of the fine gel pore formation is that the resulting inner steam pressure is much lower than in bigger pores. Furthermore, during the setting process, silica sol does not form any new chemical compounds that would impair the heating process. This leads to a minor risk for explosive spalling, because of lower mechanical stress in the matrix. Due to the lack of chemical bonded water, the process of dewatering is completed at temperatures about 100°C. Uncritical heat up with a rapid heating rate is possible, which leads to short downtimes of the kiln-aggregates. Another advantage is the excellent thermochemical behaviour. There is no CaO in the bonding matrix, so there isn't any risk for the formation of low melting phases, therefore higher maximum service temperatures can be reached. The crucial disadvantage is the low mechanical strength of silica sol bonded castables in the temperature range below 1000 °C. Before the formation of the ceramic bonding starts above 1000 °C, the modest strengths increase the risk for damages at linings or prefabricated shapes.

The importance of these properties can be explained at the blast furnace (BF), in application and at lining. In application the upper section of the BF includes the pre-heating zone. The maximum process temperature in this area is up to 400 °C. With its high strength development at temperature up to 1000 °C, the bonding with CAC is convincing at this area. The physical properties of the silica sol bonding aren't comparable to the CAC in this section. With increasing the furnace temperature in the carburation and melting zone over 1000 °C, the silica sol bonding shows its benefits at thermomechanical behaviour and durability. This disparity leads to a combined lining of aggregates like blast furnaces. To reach best performance and lifetime at all conditions, several bonding systems are necessary. This includes more expenditure at the building site, because two materials and two liquids (water and silica sol) are needed.

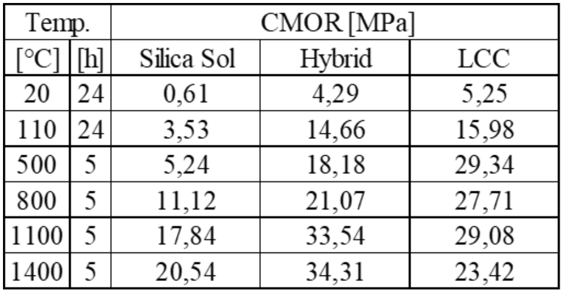
There are also technological differences at the lining process. With rising demands for time and energy saving, the need for hot installation/reparation is given. Cement bonded shotcrete installations are only possible on cold surface and low ambient temperature. The hydraulic reaction and property formation cannot take place at hot conditions. That's why the BF needs to be cooled down completely, which costs lots of time, energy and therefore money. From "hot to hot" condition it lasts several weeks. With the silica sol bonding, the possibility for hot lining is given. The chemical reaction allows to install/repair on hot surfaces and at high ambient temperatures, so the BF doesn't need a complete shutdown. In combination with modern lining techniques like robotic based shotcreting, the material can easily be served. This results in an economic and safe lining procedure.

The aim of this investigation was to develop a new bonding system which combines the advantages of both systems explained above. In the following results the properties of the Hybrid bonding systems are shown. This new system is also based on a sol binder, with additional adjustments at the dry material.

RESULTS AND DISCUSSION

The development of the cold modulus of rupture (CMOR) is shown in table 1. Figure 1 shows the properties at low temperature and figure 2 includes the whole temperature range. For all measurements, a tabular alumina-based vibration castable was chosen. The strength of silica sol, Hybrid and cement is presented after storing in climate chamber and in drying cabinet. As supposed, there was a significant increase in strength of more than 300 % in CMOR with Hybrid bonding compared to silica sol.

Tab. 1. CMOR related to binder and temperature treatment



Temp.		CMOR [MPa]		
[°C]	[h]	Silica Sol	Hybrid	LCC
20	24	0,61	4,29	5,25
110	24	3,53	14,66	15,98
500	5	5,24	18,18	29,34
800	5	11,12	21,07	27,71
1100	5	17,84	33,54	29,08
1400	5	20,54	34,31	23,42

After curing in climate chamber CMOR of silica sol was 0.6 MPa. The Hybrid samples strength increased to 4.3 MPa and the cement bonded CMOR was 5.3 MPa. After drying, there were similar trends in the results. The CMOR of silica sol was 3.5 MPa, the Hybrid's CMOR increased to 14.7 MPa and the cement's CMOR reached 16.0 MPa.

After temperature treatment (Fig. 2) at 500 °C the cement bonding had the highest CMOR with 29.3 MPa, followed by the Hybrid (18.2 MPa) and the silica sol bonding (5.2 MPa), analogous to the CMOR after 110 °C. With increase of the pre-firing temperature, the silica sol increased its strength with formation of the ceramic bonding up to 20.5 MPa after pre-sintering at 1400 °C. The cement bonded materials strength decreased with higher temperature treatment, from 29.1 MPa after 1100 °C to 23.4 MPa after pre-firing at 1400 °C. The Hybrid bonding developed a CMOR after firing at 800 °C from 21.1 MPa, rapidly increasing to 33.5 MPa after 1100 °C and finally increasing to 34.3 MPa after pre-sintering at 1400 °C.

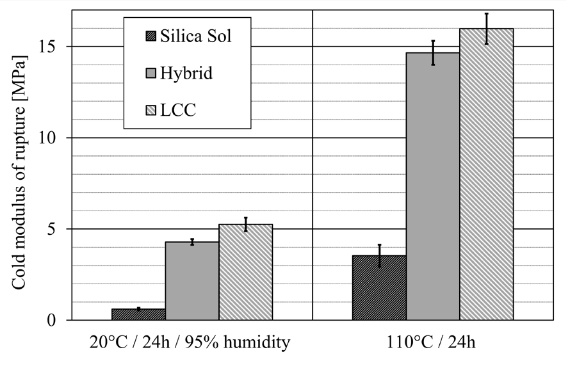


Fig. 1. CMOR after curing and drying, high green strength for Hybrid and LCC

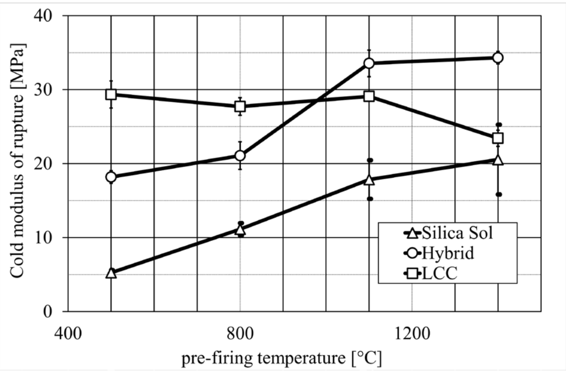


Fig. 2. CMOR according to pre-firing temperature

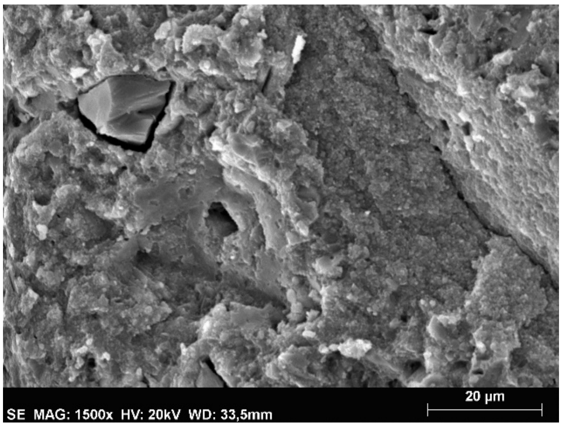


Fig. 3. SEM picture (1500x) of Hybrid fractured surface

In figure 3 the fractured surface of the Hybrid bonding is shown after curing.

A gelation of the silica sol took place, but the fractured surface looks not that smooth as the pure silica sol. Also, the surface showed sharp edges. These observations proved a modified setting process. There is still a gelation of the silica sol, but also another reaction, triggered by the added Hybrid additives. The relative gel pore content of the total porosity was measured via mercury method after drying at 110 °C /24h. The silica sol bonded sample showed a high amount of gel pores, with 54.8 %, the cement bonded sample had 37.2 % gel pores in the measured area. The highest amount of gel pores revealed the Hybrid bonded sample with 57.2 %. This was a positive result for the fast heating up properties of the castable. There are similar pore sizes compared to the silica sol bonded sample, which is well-known for its fast heating up properties [5]. In the next step quick firing tests were performed in laboratory and production scale (> 450 kg). Both samples did not show any cracks, damages, or explosive spalling after the rapid heating up procedure. The samples were heated from room temperature to 800 °C in a pre-heated oven. This test confirmed the adoption of the micropore distribution and the uncritical heating up properties for the silica sol and Hybrid bonding. The combination of silica sol and reactive additive components lead to a significant improvement of performance. The Hybrid bonding shows an increase of the mechanical strength up to 1000 °C, the possibility for rapid heating rates and an enhanced high temperature durability. This was confirmed in laboratory and in production scale in this project and could be successful transferred to practical conditions.

The opportunity for installation with shotcrete systems on hot surfaces in combination with the wide-ranging properties of Hybrid are opening great ways for the reduction of carbon emission. Maintaining and installation at high temperatures on hot surfaces are possible, so there is no extra heating necessary. In addition, the maximum heating temperature and duration can be drastically reduced compared to cement bonding. This can save large quantities of fuel (e.g. natural gas). By using Hybrid in a permanent lining, for example, the maximum drying temperature can be decreased from standard 800 °C to below 500 °C (analogous to silica sol bonding). In addition, experience shows that the drying time can be lowered by up to one third depending on the wall thickness. Thus, by reducing the temperature and duration of heating, gas consumption can be reduced by over 70 %. Depending on the drying unit, this leads to CO_2 savings from natural gas combustion of the same order of magnitude. Hybrid offers best prerequisites for future challenges with energy-optimized processes.

All these examples have already been successfully applied in industry. The possibility of producing pre-shaped components without cement bonding achieved excellent results, for example at electric arc furnace delta sections. Figure 5 shows a 4000 kg delta section made of REFRACAST® Hybrid A-72 TS, which can be transported at only four anchors after drying without further reinforcement. The combination of high strength and non-critical heating has already been convincing in the case of spouts of crucibles and ladles. These have often to withstand the impact of scrap without being heated up before the first use. The same advantages were convincing in various applications in the non-ferrous and cement sectors. In blast furnace applications, good experiences were made in runner systems and a complete blast furnace shaft was already lined with only one Hybrid shotcrete material. In all applications, the combination of fast heating, high strength and the possibility to use Hybrid bonding in almost all installation techniques, were convincing.

Fig. 5: 4000 kg EAF delta section after drying, liftable at only four anchors

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