HYBRID Technology – Advance for Sol-Gel Bonded Refractory Concrete

J. Neese, B. Kesselheim, S. Rollmann, S. Scheffler

Monolithic refractory castables can contain different bonding agents. The commonly used cement and silica sol binders have different advantages for their usage. The cement bonding with calcium aluminate cement is characterised by the development of high strength at a temperature up to 1000 °C. A general disadvantage is, that corresponding linings need to be heated up very sensitive, especially at the initial heat-up. Because of the containing calcium oxide there's also a risk of formation of low melting phases. A further alternative is the cement free silica sol bonding. It is proven, that the heating up properties aren't critical and there is no risk of the formation of low melting phases, cause of missing CaO. The probably only drawback of this system is the mechanical strength at temperatures up to 1000 °C, which can lead to a higher risk of damages of unshaped and prefabricated components. Due to several weaknesses of these commonly used binders, the aim of this project was to invent an innovative bonding system with improved properties. The focus was on high strength development over the complete temperature range, fast heating up properties and a good temperature durability. This novel HYBRID bonding system is directly compared to the both conventional used systems (CAC/silica sol). Furthermore, there should be given an overview of possible applications including outlook to further developments.

1 Introduction

In industrial processes like the production of steel, pig-iron and non-ferrous metals the use of refractories is necessary. Also sophisticated thermal applications like waste incineration or the generation of energy won't be possible without refractory products. The usage of unshaped refractory materials has main benefits in contrast to shaped refractory materials. Advantages are e.g. a straightforward installation of aggregates with complex geometries and a fast lining procedure [1]. In general, refractory linings must withstand thermal shocks and chemical and mechanical stress at high temperatures. The further development of clean steel production and the increasing demands of steel purity leads to high requirements to the refractory material. On the one hand, there shouldn't be any solving processes or damages at the refractory lining in application, also at increased temperatures. On the other hand, the lining process needs to be most economic. When kiln-aggregates like blast furnaces, melting furnaces and steel ladles are out of operation, cause e.g. maintenance, it's very expensive for the costumer. For the development of refractory castables there are different types of bonding systems available. Each system offers different advantages and disadvantages.

1.1 Calcium aluminate cement

The commonly wide used binder is Calcium Aluminate Cement (CAC) [3]. 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 [4]. The hydrates are leading to high strength, directly after setting and at temperatures below 800 °C. Another advantage is the good adjustable setting behaviour [5].
A disadvantage of this system is the chemically bonding of water in hydrate phases. The point of dewatering takes place up to higher temperatures above 500 °C [6]. This effectuate a tear off of the capillary channels, which are required to transport the water vapour 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 very sensitive heating rates. Another detriment is that calcium oxide (CaO) is included. In combination with Al_2O_3 and SiO_2, the formation of low melting phases like anorthite is possible which is adverse for the high temperature durability.

1.2 Silica sol

An alternative for the cement bonding system is the cement free silica sol bonding,

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Keywords: HYBRID, silica sol,
green strength, fast heating-up

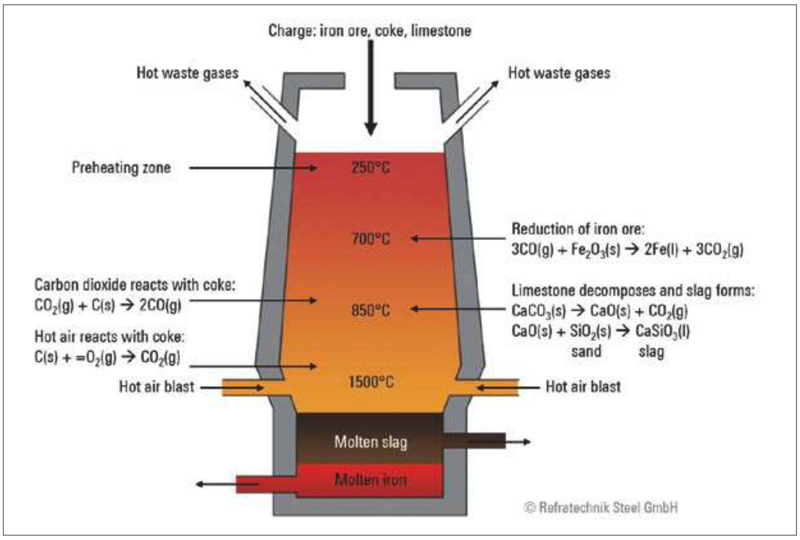

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Fig. 1 Schematic structure of a blast furnace

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 [6]. 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.

Fig. 2 Robotic shotcrete blast furnace reparation at high temperature

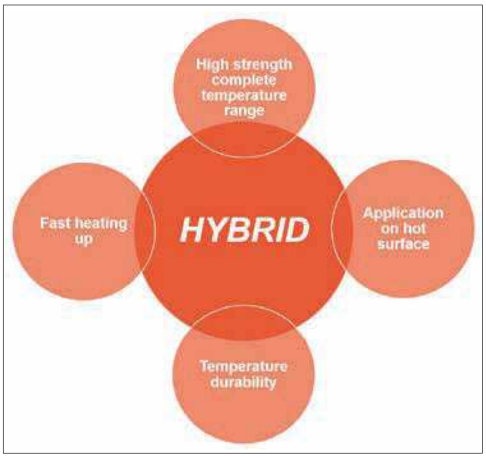


Fig. 3 Overview of aims for the HYBRID development

For the heating up process, this leads to a minor risk for explosive spalling, because of lower mechanical stress in the matrix. Compared to bonding with CAC's, the silica sol bonding has benefits, especially at high temperatures. Due to a lack of chemical bonded water, the process of dewatering is completed at temperatures of 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 is not any risk for the formation of low melting phases, therefore higher maximum service temperatures can be reached. In summary the relevant benefits in comparison to CAC's are:

- accelerated heating up rate (shorter downtimes);
- better performance at high temperature;
- improved thermomechanical behaviour;
- higher max service temperature;
- installation at hot surface/higher ambient temperatures (energy saving);
- strong sticking on refractory surface.

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 at 1000 °C, the modest development of strength increases the risk for damages at linings or prefabricated shapes.

1.3 Practical relevance

The importance of these relevant properties can be explained at the blast furnace (BF), in application and at lining (Fig. 1). 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 until 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 "hybrid" lining of aggregates like blast furnaces. To reach best performance at all conditions, both bonding systems are needed. 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 (Fig. 2). Cement bonded shotcrete installations are just possible on cold surface and low ambient temperature. The hydraulic reaction and property formation can't 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.

The BF doesn't need to be cooled down to room temperature, no platforms are necessary and there is no problem with remaining CO gas in the aggregate which could

Tab. 1 Recipe for the investigations: for LCC 7,50 % Secar71 is added, alumina amount is reduced

		Content [mass-%]
Tabular alumina	2–5 mm	25,00
	1–3 mm	20,00
	0–1 mm	20,00
	0–0,045 mm	12,50
Alumina		16,30
Microsilica		6,00
Dispersant		0,15
PP fibre		0,05
		∑ 100
Water		5,60
Silica sol		8,00

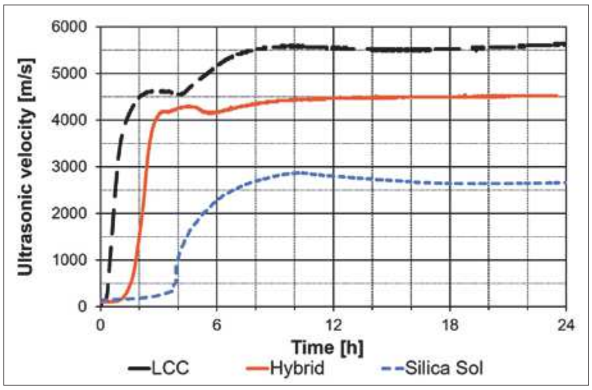


Fig. 4 Ultrasonic velocity of LCC, HYBRID and silica sol at the setting process

be dangerous for workers. This results in an economic and safe lining procedure.

1.4 Objective – HYBRID bonding system

At least the advantages and disadvantages of the commonly used bonding systems results in the goal of this study. Starting with the benefits of the silica sol bonding system, the intention was to combine these with an increase of strength between room temperature up to max service temperature. As shown in Fig. 3, a novel HYBRID bonding system should be developed, which combines the benefits of the silica sol bonding with additional high strength over the whole temperature range.

2 Experimental procedure

The HYBRID bonding directly will be compared to a Low Cement Castable (LCC) and a silica sol bonded castable. The template recipes are based on tabular alumina with a maximum grain size of 5 mm, to minimise the influence of impurities as in natural raw materials (Tab. 1). This composition is suitable to demonstrate the differences between the bonding systems. To the LCC 7,50 % Secar71 is added, this amount is reduced to the amount of alumina in this recipe. The LCC is mixed with water, the silica sol and HYBRID systems are mixed with a silica sol (30 % solid content, pH value 9,5). The samples are prepared in format B, according to DIN EN ISO 1927-5.

For the HYBRID composition, the silica sol bonding system is doped with small amounts of reactive additives, which were selected in trials before at the first part of this project. The detailed composition is protected by Refratechnik Steel GmbH/DE.

2.1 Ultrasonic test while setting

The decisive reactions for the development of green strength take place while the setting process. To investigate the changes in setting behaviour the IP8 ultrasonic measurement system by UltraTest GmbH/DE is used. After mixing, the material is stored for 24 h at 20 °C with a humidity of 95 % while the ultrasonic velocity is recorded. The increasing of velocity can be associated to the increasing of strength and Young's modulus.

2.2 Scanning electron microscope

To understand the changes regarding setting behaviour and green strength, Scanning Electron Microscope (SEM) shots were made directly after curing. To exclude the influence of temperature treatment and still get a dewatered sample for successful vacuum in the SEM, the samples were freeze-dried. This test was performed at material testing center at University of Applied Science Koblenz/DE.

2.3 Green strength

The development of green mechanical strength is tested after curing for 24 h in the climate chamber at 20 °C and a humidity of 95 % according to DIN EN ISO 1927-6 (min. six samples per bonding system).

2.4 Strength development after temperature treatment

After curing, the samples were dried for 24 h at 110 °C. Six sample per bonding system were tested directly after drying, the other samples had a heat treatment at 500 °C, 800 °C, 1100 °C and 1400 °C with a dwell time of 5 h in a Nabatherm/DE electric laboratory kiln.

2.5 Temperature durability

To measure the temperature durability the Creep Under Compression (CUC) test, according to DIN EN ISO 1927-6, were chosen. The samples were pre-sintered at 1500 °C with a dwell time of 5 h. At measurement, the samples were fired up again to 1500 °C with a load of 0,2 MPa and a heating rate of 5 K/h. The linear change ε is recorded against the sample temperature (20–1500 °C) and against the dwell time (0–25 h).

2.6 Fast heating up properties

To compare the amount of fine gel pores the micropore distribution was measured. The samples were dried at 110 °C (24 h) and the measurement took place at AMPA material testing center at University of Kassel/DE.

Additionally, a quick firing test was performed in two scales. In laboratory a sample with a weight of 12,5 kg was cured for 24 h in climate chamber. To avoid dry out, the sample was covered while curing. After demoulding, the sample was heated up with 500 K/h in an electric kiln to 1000 °C. To confirm this pre-test, another sample with a weight of 950 kg in production scale was shaped. These sample was also cured for 24 h at 20 °C and then heated up with the maximum possible heating rate (40 K/h) to 500 °C. In a macroscopic investigation, the samples were examined to cracks, damages or spalling.

3 Results and discussion

3.1 Ultrasonic test while setting

In Fig. 4, the course of ultrasonic velocity is shown while the setting process. The vel-

Fig. 5 SEM picture (1500 ×) of LCC fractured surface, bright hydrate phases visible

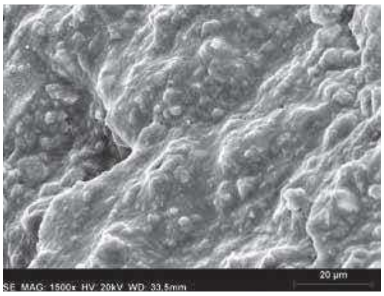


Fig. 6 SEM picture (1500 ×) of silica sol fractured surface, gelation around the grains

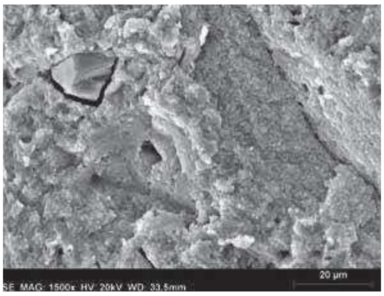


Fig. 7 SEM picture (1500 ×) of HYBRID fractured surface, modified gelation with crystalline structure

ocity of the silica sol is increasing after 4 h. There's a plateau between 2600–2800 m/s after 10 h. The cement bonding has a rapid increase of ultrasonic velocity after less than 30 min near to 4600 m/s.

Between 2–4 h elapsed time, there is a plateau. This is a characteristic course for cement bonded castables, in this period of rest there are solving processes until the hydrate phases are precipitate. This precipitation is indicated by the second rising of the ultrasonic velocity after 5 h. There is a second plateau at nearly 5600 m/s velocity after 8 h. The reaction of the HYBRID bonding which is indicated by the increasing of velocity takes place after nearly 2 h. The velocity increases to 4200 m/s after only 3 h. After a short period of deviation, the velocity stagnates at more than 4400 m/s after 8 h. These courses imply, that strength development between the bonding systems is dissimilar and that higher green strength could be reached with the HYBRID system.

3.2 SEM

In Fig. 5, the SEM picture of the cured cement bonded castable is shown. At the fractured surface bright crystalline parts are visible. These hydrate phases are responsible for high strength development [6]. There are no crystalline structures at the silica sol bonded sample (Fig. 6). The corundum grains are surrounded by a gel, which manages the setting process.

In Fig. 7, the fractured surface of the HYBRID bonding is shown after curing. There is a gelation of the silica sol, but the fractured surface looks not that smooth as the silica sol sample. Small amounts of bright materials are visible, and the surface have clearer edges.

These observations prove that the authors have a modified setting process, which may lead to higher strength development. There's still a gelation of the silica sol, but also another reaction, triggered by the added additives. In the upper left section there is a quarry corundum grain.

3.3 Green strength

The development of the Cold Modulus of Rupture (CMOR) at lower temperatures is shown in Fig. 8. The strength of silica sol, HYBRID and cement is presented after storing in climate chamber and in drying cabinet. As supposed, there is a significant increase of strength of more than 300 % in CMOR with HYBRID bonding compared to silica sol. After curing in climate chamber, CMOR of silica sol is 0,6 MPa.

The HYBRID bonded samples strength increased to 4,3 MPa, and the cement bonded ones CMOR is 5,2 MPa. After drying, there are similar trends in the results. The CMOR of silica sol is 3,5 MPa, the HYBRID's CMOR is 14,7 MPa and the cement's CMOR is 15,9 MPa.

So, the maximum strength of the cement bonding (7,5 % CAC) is nearly attained with the HYBRID bonding. The deviation is similar to the commonly used bonding systems.

3.4 Strength development after temperature treatment

After temperature treatment (Fig. 9) at 500 °C, the cement bonding has the highest CMOR with 29,3 MPa, followed by the HYBRID (18,2 MPa) and the silica sol bonding (5,2 MPa), analog to the CMOR after 110 °C. With increase of the pre-firing tem-

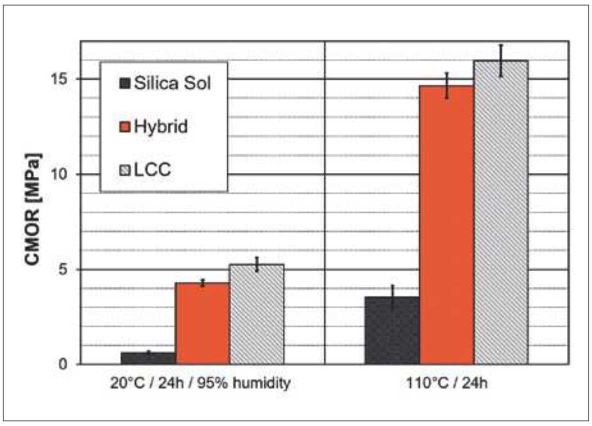


Fig. 8 CMOR after 20 °C/24 h and 110 °C/24 h, significant increase from silica sol to HYBRID bonded concrete

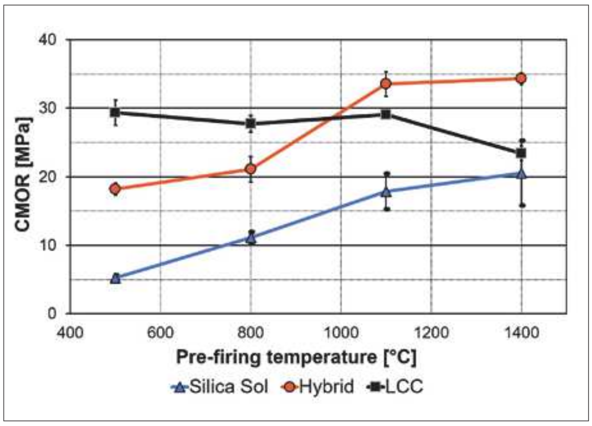


Fig. 9 CMOR up to 1400 °C, highest increase of strength of HYBRID bonding

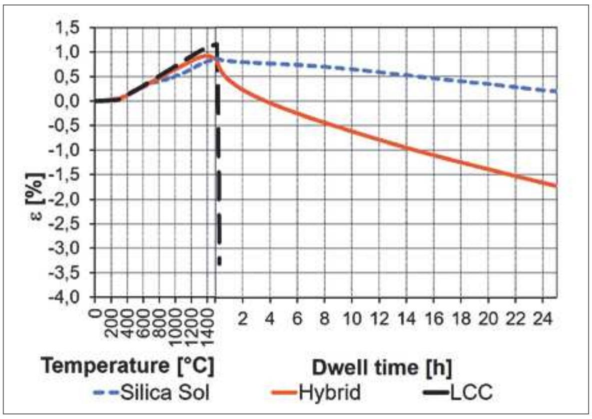


Fig. 10 Creep Under Compression (CUC) test, fast above of measurement at LCC, better performance of HYBRID and silica sol

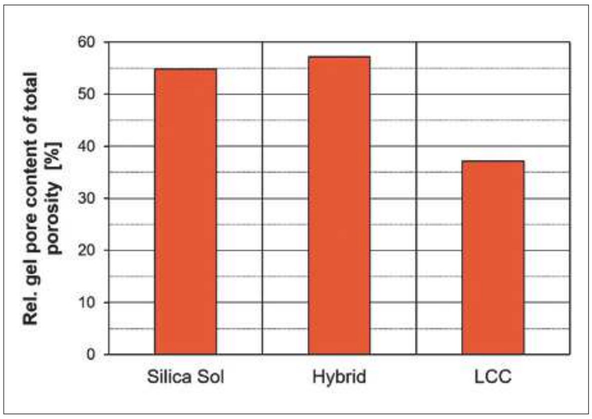


Fig. 11 Micropore distribution after 110 °C/24 h, high amount of gel pores at HYBRID and silica sol bonding system

perature, the silica sol increases its strength with formation of the ceramic bonding up to 20,5 MPa after pre-sintering at 1400 °C. The cement bonded material decreases its strength with higher temperature treatment, from 29,0 MPa after 1100 °C to 23,4 MPa after pre-firing at 1400 °C. The HYBRID bonding develops a CMOR after firing at 800 °C from 21,0 MPa, rapidly increasing to 33,5 MPa after 1100 °C and finally increasing to 34,3 MPa after pre-sintering at 1400 °C. With an increase of pre-firing temperature, there is also an increase of strength at the HYBRID bonding system. The course is like the silica sol bonding, but with a much higher increase to much higher strengths.

3.5 Temperature durability

In Fig. 10, results of CUC are shown. While heating up the samples, there is a similar extension. At the dwell time, there are significant different courses between the bonding systems based on the model recipe (Tab. 1). The silica sol bonding shows its benefit at temperature durability in this test, there is nearly no shrinkage.

The cement bonding, in due to the high amount of low melting phases, has a very high deformation in this composition. After just 5 min the test procedure must be aborted. Better durability at CUC has the HYBRID bonding, with a minor linear change over 25 h. There is no abort of the measurement at these high temperatures.

3.6 Fast heating up properties

In Fig. 11, the relative gel pore content of the total porosity is shown. The silica sol bonded sample has a high amount of gel pores, with 54,8 % in the measured area, the cement bonded sample show 37,2 % gel pores in the measured area. The highest amount of gel pores reveals the HYBRID bonded sample with 57,2 %. This is a positive result for the fast heating up properties of the HYBRID bonded castable, there are similar pore structures like the silica sol bonded sample, which is well-known for its fast firing up properties already [2].

In the next step a quick firing test was performed in laboratory and production scale. Both samples don't show any cracks, damages or explosive spalling after the rapid heating up procedure (Fig. 12). This test confirms the adoption of the micropore distribution and the uncritical heating up properties for the silica sol and HYBRID bonding.

4 Conclusion

The advantages of the novel HYBRID bonding system compared to the commonly used systems are demonstrated successfully.

Fig. 12 950 kg HYBRID sample after rapid heating up to 500 °C

Fig. 13 EAF cover plate, made of REFRACAST® HYBRID A-72 CT/S, dried and demoulded without damages, lifted at only four anchor points after curing

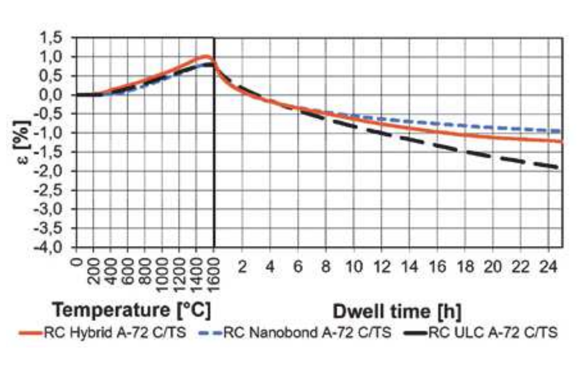


Fig. 14 CUC with practical used raw material base

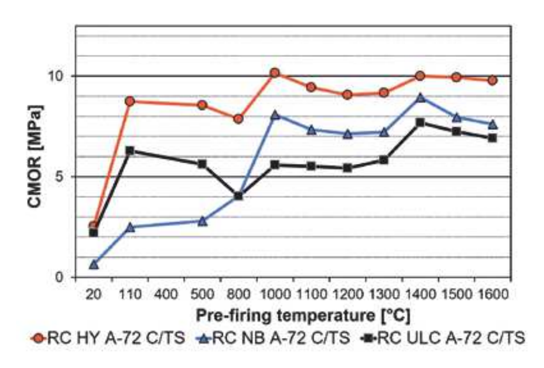


Fig. 15 CMOR of applied products up to 1600 °C

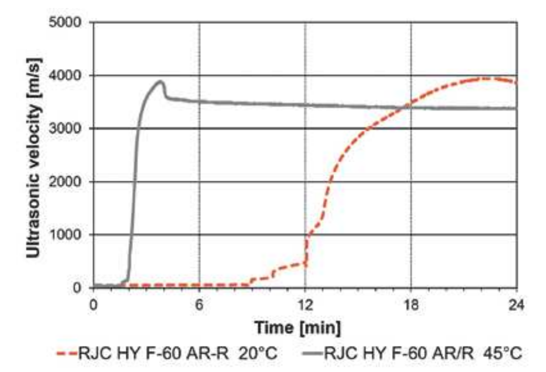
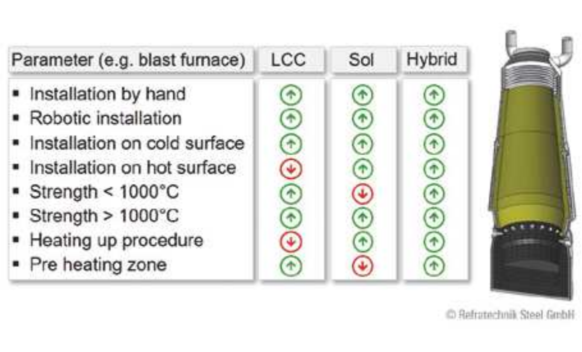


Fig. 16 Ultrasonic velocity of the HYBRID shotcrete version at higher ambient temperature (45 °C)



Parameter (e.g. blast furnace)	LCC	Sol	Hybrid
▪ Installation by hand	↑	↑	↑
▪ Robotic installation	↑	↑	↑
▪ Installation on cold surface	↑	↑	↑
▪ Installation on hot surface	↓	↑	↑
▪ Strength < 1000°C	↑	↓	↑
▪ Strength > 1000°C	↑	↑	↑
▪ Heating up procedure	↓	↑	↑
▪ Pre heating zone	↑	↓	↑

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Fig. 17 Advantages and disadvantages of the bonding system for the BF installation

The combination of silica sol and reactive additive components lead to a significant advance 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.

4.1 Outlook

In Fig. 13 there is shown an andalusite based cover plate of an electric arc furnace. This 4000 kg shaped component, made of REFRACAST® HYBRID A-72 C/TS, was demoulded and dried without any damages or cracks. It was also possible to lift it up at only four anchor points directly after curing. Also, at unshaped linings we had very good experience with HYBRID bonded concretes. In Fig. 14, the CUC of the same HYBRID bonded product is shown, in contrast to different bonding systems based on same raw materials. In comparison, the influence of the used raw materials in the model recipe becomes clear (Fig. 10). Even if the cement bonded (ULC) shows much lower deformation, the temperature durability of the HYBRID and silica sol (Nanobond) bonding system is still convincing (Fig. 14).

Another advantage was demonstrated in strength development. The increase of CMOR from 20 °C up to 1600 °C is visible (Fig. 15). At the entire temperature range, the HYBRID bonding system has a cogent strength development, which confirms the usability for high temperature application.

The next step was the up-scaling of the bonding system to more installation techniques.

There's already the possibility to use HYBRID bonding system for vibration castable (REFRACAST®), self-flowing castable (REFRASELFCAST®) and wet gunning/shotcrete material (REFRAJETCRETE®). Especially the shotcrete technique in combination with the benefits of the HYBRID bonding systems has convincing possibilities. Shotcrete material needs to withstand different, especially thermal requirements in due to surrounding temperatures. While mixing 1000 kg concrete in double piston pumps, there is an enormous input of energy because of shear forces and friction. Therefore, the material temperature increases significant and additionally, it often needs to be pumped up to heights of 70 m (e.g. BF), also at higher ambient temperatures (e.g. Latin America). While this treatment with shear forces, friction and high ambient temperatures, the wet mixed concrete must have a very long working time.

Fig. 16 compares the setting behaviour of the shotcrete material (REFRAJETCRETE® HYBRID F-60 AR/R) at ambient temperatures of 20 °C and 45 °C. At 20 °C, the material has a processing time of about 10 h, whereas even at the extreme temperature of 45 °C still about 90 min processing time is available, which can be considered as sufficiently long for this processing technology.

The opportunity for installation with shotcrete systems on hot surfaces in combination with the wide-ranging properties of HYBRID are opening great new ways in application. For example, blast furnaces don't need to be lined with two different materials, because of the temperature gradient in the aggregate. Maintaining and installation at high temperatures on hot surfaces is possible. The increased strength below 1000 °C avoids damages, expands the application possibilities and favours the production of pre-shaped components. In Fig. 17, the practical relevant properties are shown in relation to the bonding system for the lining of blast furnaces.

Generally, the installation of HYBRID by shotcreting at higher ambient temperatures and on hot surfaces is possible. Hence, much energy can be saved and there is a reduced CO_2 emission. The HYBRID materials are characterised by great performances and durability to the whole temperature range. All in all, the positive results of this study could be successfully transferred to practical conditions.

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