SOL BONDED ALUMINA SILICA MONOLITHICS–NEW DEVELOPMENTS, RECENT EXPERIENCES, AND FUTURE POSSIBILITIES

Milos Blajs[1], Bernhard Pribil[1], Gerald Reif[1]
[1]RHI AG, R&D Alumina Monolithics, Leoben, Austria

ABSTRACT

In the last years a new generation of castables, shotcreting, and gunning mixes with colloidal silica bonding technology has provided enormous advantages in terms of processing and material properties, the most important being an easy-drying behavior, excellent thermal shock resistance, low brittleness, as well as hot erosion and corrosion resistance. As a consequence, in many different industries these materials show significant performance improvements and lifetime increases compared to commonly used cement bonded castables. Nevertheless, continual research and development efforts in the field of Sol bonded monolithics have lead to further improvements and innovations. The colloidal silica binding system provides the basis for further developments in the area of novel and innovative carbon containing as well as carbon-free refractory matrix designs for alumina monolithics.

Furthermore new developments on the liquid binder itself provide major improvements in terms of handling and logistic aspects. To date, the liquid Sol binder had the disadvantage of being irreversibly destroyed when frozen. To overcome these drawbacks a special frost protected Sol binder, that allows storage and transport even below -30 °C, has been developed.

INTRODUCTION

Due to some specific features, Sol bonded monolithics have become more and more popular in various refractory applications. The liquid colloidal silica binder is transported separately from the castable and mixed with the dry material shortly before installation.

Contrary to common conventional and low cement castables (LCC), these mixes counteract the disadvantage of time consuming drying procedure by providing a faster, easier, and safer dry out behavior. In addition, the binder dosing is easier and setting is less sensitive at different ambient temperatures. The dry mix does not contain any binder, which provides advantages in terms of shelf life and storage. With 18 months for both, the dry mix and the liquid binder, the shelf life of Sol bonded products is considerably higher than common low cement castables.

Furthermore, the Sol bonded monolithics feature many improvements in terms of performance and durability, compared to the widely used hydraulically bonded products. Superior thermal shock resistance, reduced brittleness, improved refractoriness, and abrasion resistance at elevated temperatures, as well as high resistance against alkali attack, are some of the advantages which lead to the outstanding performances in highly loaded application areas. In some applications the lifetime was at least tripled [1].

Additionally to castables, a wide range of Sol bonded gunning mixes have been introduced to the market. These materials can be installed using common conventional gunning equipment.

The dry gunning method is a very simple, flexible and cost effective installation method in terms of machinery demand. However, there are further gunning methods, namely shotcasting and shotcreting for installing large amounts of monolithic, that can now also be used with Sol bonded products. For these installation methods, that enables installation rates up to 10 tons per hour, the Sol bonded vibration castables were adapted to improve their pumping properties, mainly to reduce friction in the pipes and hoses.

As such, a well established and extensive product portfolio is available on the market, covering a wide range of raw material concepts and all commonly used installation methods.

Up to now the sensitivity of the liquid binder to freezing temperatures was a distinct disadvantage. To overcome this problem research and development projects focused on the development of a frost resistant colloidal silica binder, which was introduced in 2016.

Furthermore, the special reactive small scaled particles introduced via the liquid binder and the significantly different pH values of the mixture compared to cement bonded mixes, are the basis for further developments in terms of special matrix design via in-situ phase formations at elevated temperatures.

CARBON CONTAINING SOL MIX WITH INNOVATIVE MATRIX DESIGN

Extensive research efforts in the field of carbon addition to special Sol bonded refractory castables have lead to some major improvements in relevant material properties for applications in the hot metal and steel industry.

Very complex reactions between different carbon carriers, special fine grained matrix components, and reactive small scaled particles from the Sol binder generate a special in-situ refractory matrix with superior characteristics at very high temperatures. The special mixture of various oxycarbides in the matrix, which is formed by the influence of heat, is responsible for some superior material properties. Fig. 1 shows this material under a reflected light microscope, the special in-situ formed matrix structure appears as various fine grained vitreous phases.

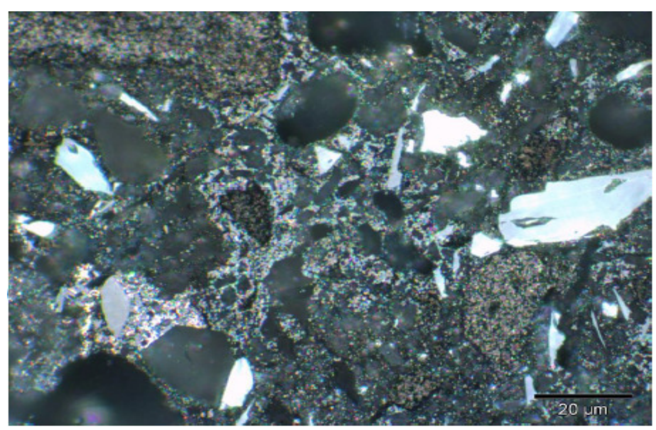

Fig. 1: Carbon containing Sol mix in a reflected light microscope; matrix with various oxycarbides, formed in-situ after heat treatment.

When compared to LC bonded castables based on the same raw materials, these carbon containing mixes demonstrate a 200-300 °C higher refractoriness under load (Fig. 2), despite the significant amount of SiO_2 which is introduced via the liquid binder. From this point of view, the bauxite based material combined with this innovative matrix design, exhibits better refractoriness under load than a LC castable based on sintered alumina.

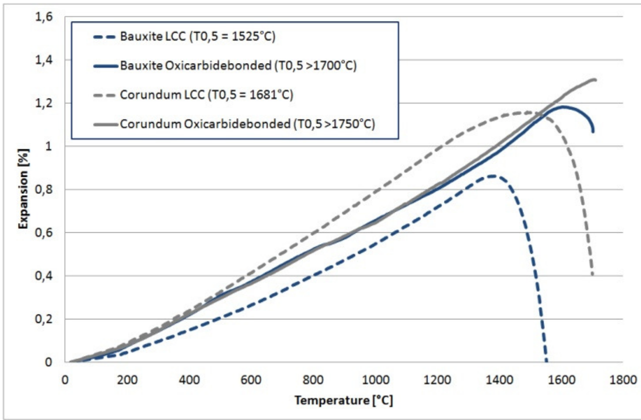

Fig. 2: Refractoriness under load after firing at 1500 °C of the novel carbon containing oxicarbide bonded castables based on sintered alumina and bauxite, compared to LC castables with the same raw materials.

Outstanding hot modulus of rupture values (>20 MPa at 1500 °C for the high alumina mix) have also been measured and indicate the considerably higher hot strengths and refractoriness.

The presence of carbon in different forms in the matrix, in combination with the microporous structure lead to a product with more ductile characteristics, which varies distinctly from the very brittle nature of traditional sintered ceramic materials. The presence of carbon also eliminates the formation of glassy phases, while the micropores inhibit cracks from propagating.

Another significant characteristic of this novel refractory material is that under oxidizing conditions it shows only a thin decarburized zone of a few millimeters below the surface. Due to the carbon content, the wettability by steel, hot metal, and slags is strongly reduced compared to common LC and ULC castables. This property results in a much higher corrosion and infiltration resistance, including a reduced infiltration depth.

Similar to standard Sol bonded castables, also in this case the Sol binder creates a completely different pore structure. The matrix structure is micro porous with an average pore size approximately one-tenth that of traditional cement bonded systems. This results in completely different material properties and facilitates water evaporation.

Several examples in steel applications with very demanding conditions had proven, that this novel material concept can set new standards in terms of performance improvements. The very aggressive operation conditions of the composition adjustment by sealed argon bubbling-oxygen blowing (CAS-OB) process in the steel production represent a good example for the potentials of this material. During this process it is possible to add all the necessary alloying elements into the melt through a slag-free surface in a controlled atmospheric environment. This is achieved by immersing a refractory bell into the steel bath above an argon purging element. The bell also enables oxygen to be lanced simultaneously with the addition of aluminum. In the resulting exothermic reaction, Al_2O_3 is formed and considerable amounts of heat are generated. It is estimated that temperatures of approximately 2000 °C can be reached inside the bell. Furthermore, the continuous cooling during the treatments and the repeated dipping into the steel bath provides heavy thermal cycling and temperature shocks to the refractory material. The new Sol bonded carbon containing material provides impressive lifetime increases for the CAS-OB bell. Compared to standard cement bonded castables the number of cycles were at least doubled. Fig. 3 shows the hot CAS-OB bell after a treatment. Clearly visible is the nonwetting property of the new carbon containing mix against slag, this feature, in addition to the significantly higher refractoriness and the thermal shock resistance is the reason for the superior performance.

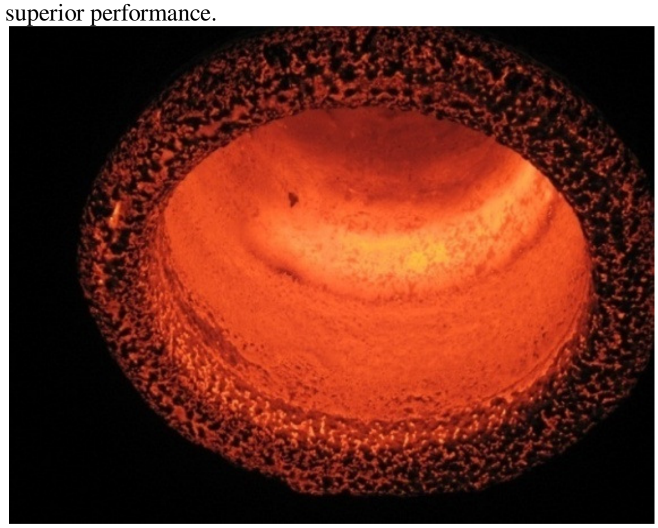

Fig. 3: CAS-OB bell with oxicarbidebonded Sol mix after steel treatment. Clearly visible is the nonwetting effect.

CARBON-FREE SOL MIX WITH INNOVATIVE MATRIX DESIGN

The successful introduction of the Sol bonded refractory castables also provided the basis for another innovative development – the mullite bonded Sol mixes. The special material design of this new refractory castable is characterized by following:

- The chemical composition and the type of the matrix components in the primary material are specially adjusted for an effective in-situ formation of a specific mullite morphology at elevated temperatures in service.
- The special micro porous structure of the strongly bonded in-situ formed matrix is responsible for the extremely low brittleness of the final material in spite of the very high refractoriness and extremely high strengths (>200 MPa) over a broad temperature range.

These characteristics make the product highly suitable for EAF-delta applications where high temperature load and thermal shocks are common.

Fig. 4 shows an overview of the microporous matrix between grains of sintered alumina after treatment at 1500 °C.

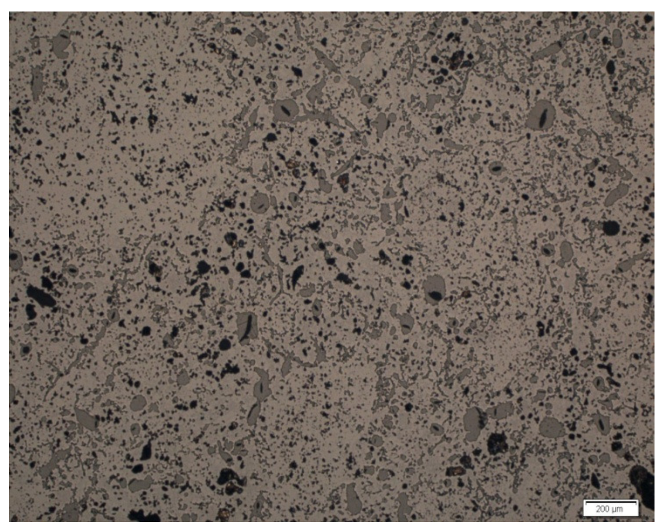

Fig. 4: Matrix overview of the mullite bonded castable after 1500 °C firing.

This novel matrix concept leads to significantly improved lifetimes in EAF-delta applications. Currently more than 50 customers have utilized these outstanding material properties and compared to common cement bonded castables, the increase in product lifetime is often 50 to 120%.

Due to the very successful application results of mullite bonded mixes based on sintered alumina, continuative development focused on usage of bulk raw materials with lower qualities, such as bauxite and fireclay. Especially with fireclay used as the main raw material in this mullite bonded castables based on Sol gel binding technology, the capability of this novel matrix design is shown by exceptional physical properties, in particular hot modulus of rupture (Tab. 1).

Tab. 1: Physical properties, low cement versus mullite bonded castables. Both mixes based on fireclay with 45% Al_2O_3 as bulk raw material.

		LC-Fireclay castable	Mullite-Matrix Fireclay mix
110 °C	PLC [Lin%]	-0.01	-0.01
	CMOR [MPa]	9.1	7.1
	CCS [MPa]	51	43
	BD [g/cm³]	2.41	2.43
	oP [Vol%]	10	12
1500 °C	PLC [Lin%]	-0.82	**0.4**
	CMOR [MPa]	21	20
	CCS [MPa]	140	**230**
	BD [g/cm³]	2.43	2.45
	oP [Vol%]	12	14
1300 °C	HMOR [MPa]	10	20
1500 °C	HMOR [MPa]	0.3	**15**

When compared to LCC's based on the same raw material or even with higher grades such as bauxite, the mullite-bonded Sol mix demonstrates a significantly higher refractoriness under load (Fig. 5).

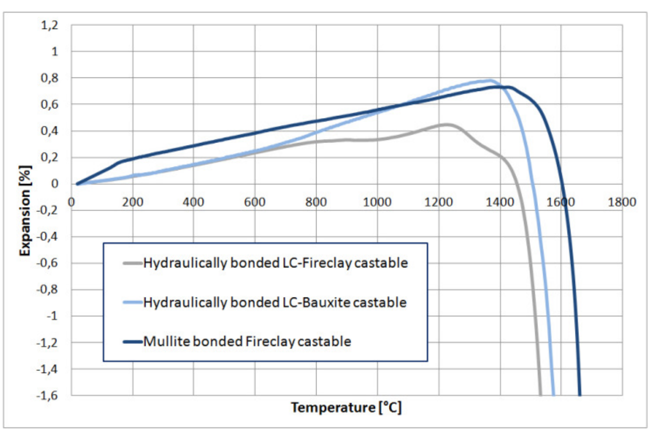

Fig. 5: Refractoriness under load; LC and mullite bonded castables based on fireclay type 45, LC castable based on bauxite. The in-situ formation of the mullite matrix provides an extraordinary high RuL

Based on the observations and results from the laboratory, an initial field trial with the mullite bonded castable based on fireclay as a prefabricated EAF-Delta was conducted. The standard lifetime was easily reached, but with higher remaining thickness of the delta after use (Fig: 6).

Fig. 6: Mullite bonded castable with fireclay; EAF-Delta with reduced costs and at least same performance.

The benchmark in this case was a low cement castable (LCC) based on bauxite. Due to the cheaper fireclay, the material costs are approximately 30% lower for this mullite bonded castable.

FROST PROOF COLLOIDAL SILICA BINDER

Up to now the liquid binder, a colloidal silica solution that is used in combination with the delivered dry Sol mixes, had the disadvantage of being irreversibly destroyed when frozen (Fig. 7). This led to an increase in logistical requirements such as cost intensive thermal transport and temperature controlled storage at the customer sites.

Fig. 7: Colloidal silica fluid after freezing and thawing – irreversible destruction due to frost.

These restrictions have retarded the utilization of Sol mixes especially in regions where cold temperatures are common and during the winter season. To overcome this drawback and to ensure the Sol bonded monolithics are accessible for all consumers and to simplify the logistics of the binder transport and storage, further R&D efforts focused on the development of a technical solution.

It is very common to add mono or divalent alcohols to water based liquids and to achieve frost protection. In the most cases this protection is limited to a specific temperature and a certain period of frost influence. However the amount of alcohol addition to the liquid Sol, which would be necessary to achieve a frost protection for example untill -30 °C for a period of several weeks, is very high. This leads to a strong dilution of the Sol and the binding effect in the refractory castable decreases significantly. The target was to develop a liquid Sol binder with frost proof properties for very low temperatures (e.g., -30 °C) without lowering the binding properties and strength of the Sol mixes. As a result of this, a new liquid Sol binder was introduced in 2016, which has a lower freezing point (-5 °C) and most importantly is not destroyed through freezing. After thawing it returns to the stable colloidal silica fluid, which can be used as a binder for Sol mixes without restrictions. It was established in numerous experiments, that this behavior is consistent for short term, long term, and cycling freezing conditions at various temperatures below 0 °C (-5, -15, -35 °C). Additionally long term exposure of larger volumes at temperatures around the freezing point, maintaining the material in a semi frozen state, did not result in harm to the product.

The newly developed frost proof Sol binder was tested with the whole range of Sol mixes. The amount of binder required and the workability concerning mixing, casting, gunning, shotcreting, and setting was not influenced. In Tab. 2 major results of some of these tests are shown. It can be seen that properties of the Sol mixes with different raw material concepts are not influenced when using the new frost protected fluid.

Tab. 2: Physical properties standard versus frost proof Sol binder.

Sol mix	Sol binder	CCS [N/mm2]		Abrasion resistance
		110°C	1000°C	[cm^3]
Fireclay type 60	Standard	62	122	5.8
	Frost proof	54	129	6.0
Fireclay type 60 and SiC	Standard	66	153	6.1
	Frost proof	62	155	5.7
Bauxite	Standard	62	142	4.5
	Frost proof	50	153	4.7

Additional tests were carried out with the frost protected Sol that has been frozen 5 times at different temperatures to investigate possible influences due to freezing. As shown in Tab. 3, it was demonstrated that multiple freezing cycles do not harm the liquid binder and final properties of mixes are unaffected.

Tab. 3: Sol bonded mix based on fireclay type 60 and SiC with untreated Sol binder and after various freezing/thawing cycles.

Sol mix	Frost proof Sol binder treatment	CCS [N/mm2]		Abrasion resistance
		110°C	1000°C	[cm3]
Fireclay type 60 and SiC	untreated	62	155	5.7
	5x 24h -5°C	58	156	6.3
	5x 24h -35°C	59	151	6.1

Fig. 8 shows an example of the hot properties of Sol mixes when using the new frost proof Sol liquid binder.

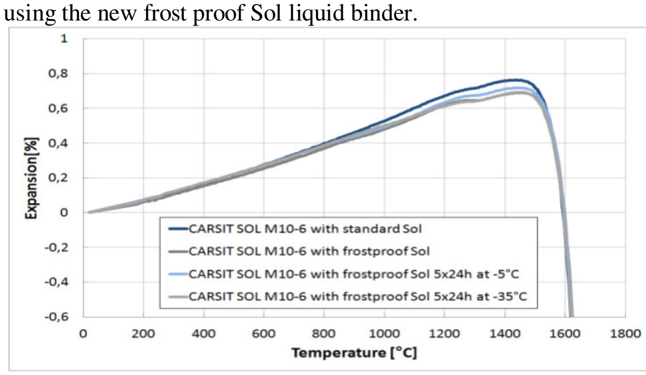

Fig. 8: Refractoriness under load, Sol bonded castable with standard Sol and new frost proof Sol binder.

Untreated and previously frozen liquid Sol samples were utilized. The results shown in the refractoriness under load curves (according DIN 51053/1) are almost identical which establishes the interchangeability of the new frost proof binder with the standard liquid and the tolerance towards freezing of the new product.

To establish the behavior of the new frost proof Sol binder for dry and wet gunning/shotcreting applications a series of gunning trials were conducted at a gunning test rig. The results show that no difference in gunning behavior and material properties between standard Sol binder and frost proof version could be detected.

For a better optical differentiation the new frost proof Sol binder has been dyed blue. The blue color can easily be seen through transparent IBC containers and canisters, which should prevent a mix up with standard Sol binder during logistic processes (Fig. 9).

Fig. 9: Blue colored frost proof Sol binder compared to white colored standard Sol binder.

In the meantime several practical experiences have been gained at various customer sites, with the usual excellent feedbacks regarding workability and material performance.

CONCLUSIONS AND OUTLOOK

The Sol bonded refractory castables are an emerging, extraordinary successful, and steadily growing product group within the area of alumina monolithics. It has been shown that due to their unique properties the Sol mixes set new standards in different fields of applications. Continuative research and development activities in the field of carbon containing and carbon free silica Sol bonded materials lead to novel refractory matrix designs with superior properties. The impressive results from the laboratory and the field indicate, that further research focused on these new material concepts, could lead to tremendous advantages regarding cost-performance ratio for different application areas in future.

With the launch of the newly developed frost proof Sol binder a technical solution has been provided, that does not require thermal transport and ensures easier handling at customer sites. This product provides a significant improvement in terms of ease of application and eliminates the major barrier for the use of the technically superior Sol bonded mixes worldwide.

REFERENCES

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Corresponding author:
Milos Blajs, milos-michael.blajs@rhi-ag.com