

WHAT IF WE DID NOT HAVE TO DRY TROUGH AND RUNNERS CASTABLES ANYMORE?

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ABSTRACT

The constant increase in demand has imposed to the steel industry an intense search for high productivity. Following this trend, the use of monolithic refractories is growing significantly, allowing shorter installation times and consequently greater availability of equipment. The main disadvantage of this class of material is the need for long drying times during its application. In this work, an entirely novel binder system for monolithic refractories is proposed, aiming at the reduction and potential elimination of the drying step during trough and runners repairs. For this purpose, this binder system was evaluated in an Al_2O_3 -SiC-C castable and compared with the two most used commercial binders: calcium aluminate cement and colloidal silica. The results showed that this system successfully produced a permeable gel-like microstructure, which led to an excellent drying behavior, even in the most aggressive heating conditions, without damaging the product's mechanical, oxidation and corrosion resistance. In the field, runners have already operated successfully using the new binder without any drying step, maintaining their performance with the benefit of a drastic reduction in repair time. Such positive results highlighted that the use of such exclusive binder could lead to the avoidance of up to 500 tons of CO_2 emitted into the atmosphere annually per blast furnace.

INTRODUCTION

The global scenario is challenging for steel producers. The low quality of raw materials, as well as the need for low coke rate and the search for green steel and high competitiveness have increased the stress and pressure for productivity and stability. Therefore, there is a search and incentive to develop products that facilitate and eliminate production steps that bring risks, uncertainties and increase manufacturing stresses.

In this trend, Shinagawa Brasil has developed a new line of monolithic products for trough and runners that do not require drying: the BestDrying^{TR} refractories. The working lining refractories in this equipment, which are in direct contact with the pig iron and slag, are traditionally monolithic materials as they allow a fast installation rate, ensuring shorter repair times and consequently higher productivity for the blast furnaces. One of the main issues when it comes to monolithic materials is the drying time required during their application. This is a determining factor in the choice of the binder used for these materials. Historically, the most used binder for monolithic refractories is calcium aluminate cement (CAC), due to its elevated green mechanical properties, suitable cost-benefit, and high chemical stability when in contact with molten metal and slag. The increase in temperature during refractories operation results in morphological and volume changes of the unit cell of the hydrated phases generated during reaction of the hydraulic cements.[1] These changes are caused by the gradual loss of water molecules generating embrittlement of the microstructure and increased internal stresses (vapor pressure). If the generated pressure exceeds the material's mechanical strength, a serious damage on the just-installed material occurs, leading to loss of the refractory integrity, risks of explosion and accidents involving operators and a large financial loss. To minimize these risks, the refractory industry has been using long heating curves for the castable dry-out, so that the dehydration of the cement can gradually take place. When large volumes of castable are applied (general repairs) the required drying time reaches several hours, accounting for approximately 30% of the total trough and runners repair time. In general, such drying stages are carried out using natural gas burners, which results in a significant consumption of this fossil fuel and, consequently, in the emission of greenhouse gas impacting on the carbon footprint of the final steel.

As an alternative to cement and its inherent drying issues, another type of binder widely used for refractory castables is colloidal silica (CS). Whereas hydraulic cements provide castables with mechanical green strength via the formation of crystalline hydrates, colloidal silica fulfills this role by forming a 3D network of permeable structure, which guarantees a much easier drying step, with less risk of explosion [2]. However, the presence of silica in most commercially applied refractories causes the generation of a low viscosity glassy phase resulting in reduced refractoriness and low resistance to chemical attack. Moreover, the use of colloidal silica as binder also generates a castable with challenging workability, due to the instability of the colloidal suspension, besides requiring additional transportation costs.

Therefore, the objective of this study was to develop an innovative and high-performance line of products (BestDrying^{TR}) which is easy to dry without bringing along the drawbacks related to the increased silica content. By the introduction of such novel technology in the market, a significant reduction on the drying curves, and consequently on the natural gas consumption, is expected during the casting house repair procedures, leading not only to a higher trough availability, but also to lower CO_2 emission rates, increased productivity, operational stability, and safety.

MATERIALS AND METHODS

To fulfil the objectives proposed in this work, a standard formulation of through and runners castable (Al_2O_3 -SiC-C) was used as the reference for the comparative evaluation of the new proposed system (BestDrying^{TR}) with the two most traditional binder systems: calcium aluminate cement (CAC) and colloidal silica (CS), as highlighted in Table 1. The amount of colloidal silica used was selected to ensure similar levels of flowability for all castables in the study.

Tab. 1: Formulation of the materials evaluated in this work containing three different binders: calcium aluminate cement (CAC), colloidal silica (CS) and the newly developed BestDrying^{TR}.

Raw Material (%wt)	Calcium Aluminate Cement (CAC)	Colloidal Silica (CS)	BestDrying ^{TR}
Alumina	56	56	56
Silicon Carbide	25	25	25
Carbon sources	3	3	3
CAC 70% Al_2O_3	2	-	-
CS 40% solids	-	10	-
BestDrying ^{TR} system	-	-	2
Others	14	14	14

The material's workability was determined by two different measurements: the flowability after mixing and the setting time at 60°C. These two tests are very important as they directly influence the final quality of the samples, as well as the applicability and performance of the refractory at field. The flowability directly influences the material's ability to flow and occupy all cavities and spaces of the region where it will be applied. The setting time determines how much time is required for the material to completely harden and to develop enough mechanical strength to allow the mold to be withdrawn. These properties present crucial importance during the through and runners repair, as they affect the final quality of the working lining, mainly its surface finishing and porosity. The flow values were obtained according to the NBR 13320 standard, where the castable is poured into a mold with well-defined diameter and the flowability is measured after removing the

mold and vibrating the material, comparing the original and the final diameters. For this test, the castable was obtained using a planetary mixer by performing the processing step according to an internal mixing procedure. The same procedure was used to produce samples for permeability, cold crushing strength and fast drying tests.

For permeability measurements, disc-shaped samples measuring approximately 5,7 cm in diameter and 2,1 cm in thickness were tested in an experimental apparatus for permeability using ambient air as the fluid. Tests were performed on three samples of each composition and two tests were performed on each sample. The Darcian permeability or viscous constant (k_1) was obtained using the Forchheimer's equation. [3]

To analyze the microstructure formed during the curing step of the proposed new binder system, scanning electron microscopy (SEM) evaluation was performed on polished and gold-coated cubic specimens (2 cm) of the castable after molding and curing at room temperature.

The cold compressive strength was measured according to the NBR 11222 standard. Prismatic samples (160mm x 40mm x 40mm) were casted and after 24 hours curing at ambient temperature, the samples were dried at 110°C and fired at 1450°C at reducing atmosphere, cooled down and tested.

For the fast-drying test at lab scales, 100mm x 100mm cylinders were prepared and cured for either at room temperature for 24h or at 60°C for 3h or 6h and immediately exposed to a temperature of 1000°C for 30 minutes. For the industrial scale test a 500mm x 600mm x 700mm block was molded, cured for 24 hours at room temperature, and directly inserted into a gas burner oven programmed to reach 400°C in a very short time (2h30min). For both lab and industrial tests, a visual inspection was carried out in the samples to check the presence of any damages generated during the fast-drying procedure, such as cracks, chipping, and/or explosion. Only the formulations with no issues during the laboratory test were tested on an industrial scale.

The castable containing the novel binder system was also installed in some casting houses in a Brazilian steel mill to run pilot trials and confirm the results attained at lab scale. The initial field tests were performed in three stages. The first stage consisted of a 50% reduction of the traditional drying curve used in the runners after repair, while in the second stage a 75% shorter curve was performed, finally, the last step consisted of eliminating the drying curve.

RESULTS

Laboratory and industrial scale results

Table 2 presents the water (or colloidal silica) content, the flow values, and the setting time at 60°C for the three evaluated formulations. Calcium aluminate cement-bonded castables, in general, present good workability, with very suitable flowability (165 mm) and setting time (100 min). The colloidal silica-bonded castable, as expected, showed an unstable behavior, with flow rate of 154 mm and setting time of 45 min, even using 10% of colloidal silica which provides a residual water content of 6%. The material bonded by the new BestDrying^{TR} system showed very similar characteristics to the reference CAC castable, pointing out that this new solution would not bring any issues during the material installation at field.

Tab. 2: Water and Colloidal Silica Content, Flowability and Setting Time at 60°C for CAC, CS and BestDrying^{TR} castables.

Material	Water / Colloidal Silica Content (%)	Flowability (mm)	Setting Time - 60°C (min)
CAC	5,6	165	100
CS	10	154	45
BestDrying ^{TR}	5,6	165	110

CAC and BestDrying^{TR} castables were prepared using water, while CS were prepared using 40%-solids colloidal silica.

The presence of hydrated crystalline phases in the CAC-bonded formulation resulted in very low permeability over the entire temperature range (110-400°C), with a permeability constant (k_1) always equal to or less than $0,1 \cdot 10^{-14}$ (Figure 2). As also expected, and previously reported [2], the permeability results illustrate the benefits of colloidal silica, which helps to generate a more permeable structure when compared to CAC. However, although representing the state-of-the-art technology, the k_1 values of the CS material was still not as high as the one attained by the very special structure formed by the BestDrying^{TR} bonding system, which resulted in a castable with extreme levels of permeability, showing a k_1 constant up to two orders of magnitude greater than the CAC formulation.

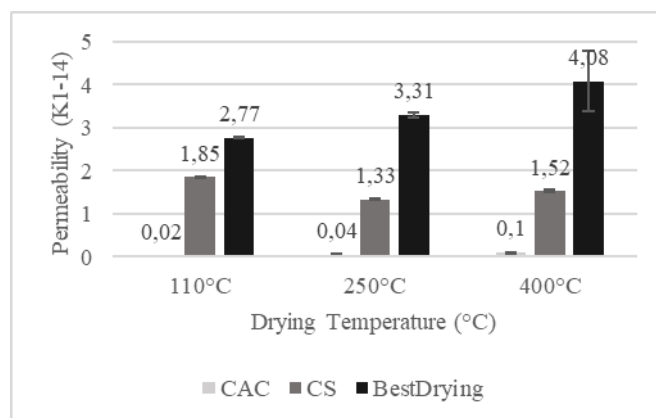


Fig. 1: Permeability test comparing the permeability constant k_1 of CAC, CS and BestDrying^{TR} binders treated at different temperatures (110°C, 250°C and 400°C).

To better understand the differences in the microstructural evolution of CAC and BestDrying^{TR} during the castable curing step, scanning electron microscopy (SEM) analyses were conducted with samples of both formulations (Figure 2). For the CAC composition (Figure 2.a), it is possible to observe the presence of countless needled crystals, resulting from the CAC hydration process and responsible for providing green mechanical strength to the sample. Numerous hydrated phases can be formed during the hydration of CAC ($CAH_{10}+AH_3$ (gel), $C_2AH_8+AH_3$ (gel/crystal), $C_3AH_6+AH_3$ (crystal)), and their formation tendency is dependent on the time, temperature, and water content present in the medium. [4] When observing the microstructure of the BestDrying^{TR} - bonded castable (2.b)), it is possible to notice a completely different structure, where an interconnected gel structure is formed throughout the material, with the absence of needle-like crystalline phases. This difference presents a direct impact on the permeability results presented above for the two materials.

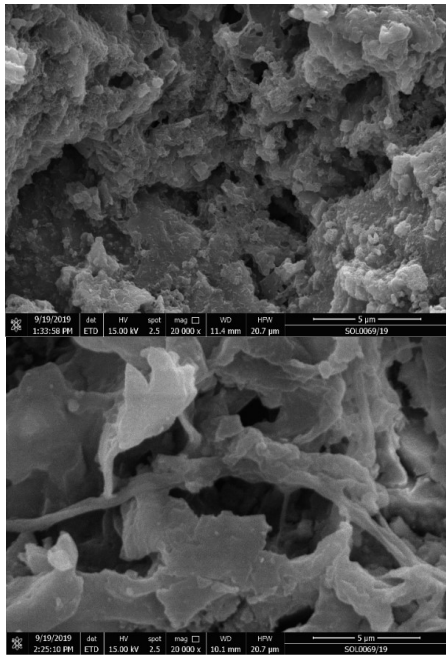


Fig. 2: Scanning electron microscopy of the formulation bonded by a) CAC, showing the presence of several needed phases, resulting from the cement hydration process; and b) BestDrying^{TR}, with the formation of a gel structure that permeates the entire sample and the absence of crystalline hydrates.

Although it is not a direct demand during use, the mechanical strength is an important parameter for trough and runner materials, as it determines, together with permeability, the drying resistance of the material. Usually when increasing the permeability of a refractory, the mechanical strength is lost, resulting in poor resistance to drying and making the development of a fast-dry material a very tough task. However, that issue was successfully overcome for the new proposed binder (Fig. 3.), as it was able to show proper mechanical strength both after drying (110°C) and firing (1450°C), with values close to those presented by the standard CAC-bonded formulation. The samples prepared with colloidal silica also presented high CCS values, but that was associated with the use of higher amount of binder required for an adequate flowability. As permeability is a property directly related to porosity, it is natural that the system with greater permeability presents greater porosity, however, the BestDrying^{TR} system was carefully developed so its greater porosity did not affect its performance in the field, as will be seen below.

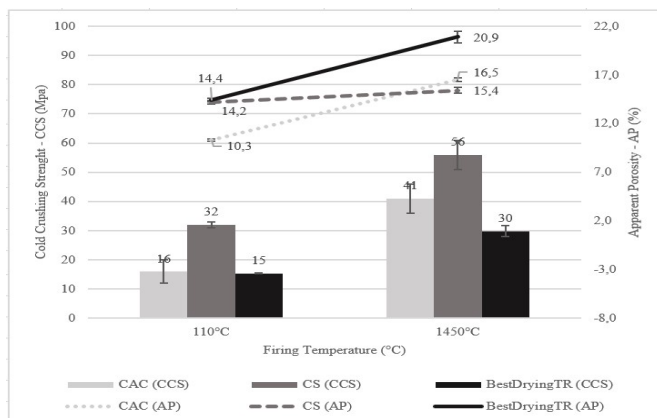



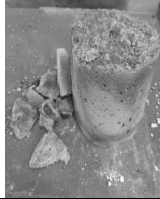
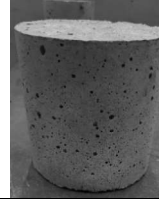
Fig. 3: Cold Crushing Strength (MPa) and Apparent Porosity (AP) of the castables bonded with CAC, CS and BestDrying^{TR} after dried at 110°C and fired at 1450°C.

The drying resistance, as mentioned above, is a result of the combination of permeability and mechanical strength. If the water

vapor is not properly released in a non-permeable structure and generates a high internal pressure which overcomes the material's mechanical resistance, it will not resist and will fail during the drying step. Therefore, an efficient fast-drying material should present high permeability, which will facilitate water vapor release, and high mechanical strength so that the internal pressure will always be lower than the castable's bonding structure.

As can be observed in Table 4, the CAC-bonded castable presents good mechanical strength, but poor permeability resulting in a material with difficulty in drying, which failed catastrophically and exploded during the tests. The CS castable, despite showing higher permeability than the CAC one, still did not present enough combination of properties and it was also damaged during the critical drying test. As a result of the very high permeability and adequate mechanical strength, the BestDrying^{TR} material did not present any external or internal damage after the fast-drying test.

Tab. 3: Fast-drying tests results presented by the castable bonded by CAC, CS and BestDrying^{TR} after curing at room temperature for 24 hours and then exposed to 1000°C for 30 minutes. Only the BestDrying^{TR}-bonded material resisted.

Time	CAC	CS	BestDrying ^{TR}
24 hours of curing			
	Severely damaged	Damaged	No damage

After successfully going through all the validation steps in the lab scale, an industrial test was performed for the BestDrying^{TR} formulation using a 500 mm x 600 mm x 700 mm block, in order to evaluate if the drying resistance of the material could be affected by any volume effect. The block passed the industrial fast-drying test again without presenting any damage in its structure, as shown in Fig. 4, indicating that the BestDrying^{TR} binder system proved to be extremely resistant to quick drying procedures, regardless the material volume.



Fig.4. Industrial scale block of approximately half a ton prepared with BestDrying^{TR} bonded castable after fast drying test.

Regarding the main properties for trough and runners' materials at high temperatures, such as the oxidation and corrosion resistances, the BestDrying^{TR} bonded castable also showed excellent results. Fig. 5 depicts the oxidation and corrosion behavior of the three evaluated formulations, where one can note that the engineered microstructure developed by the new binder during curing guarantees a low oxidation rate and low corrosion rate, even with high porosity values, which will allow it to keep good performance during use.

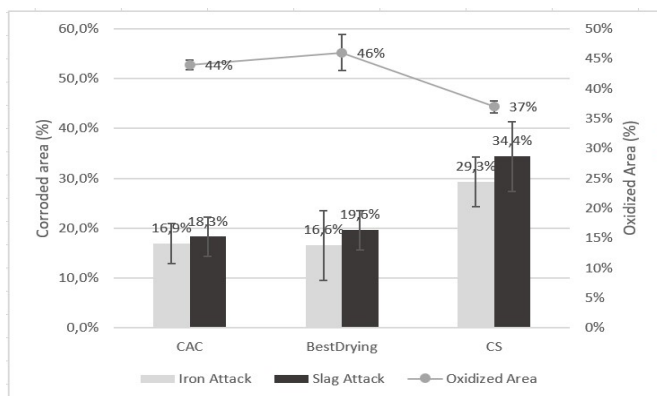


Fig. 5. Corrosion and Oxidation tests results of the evaluated formulations. Note the similar performance of CAC and BestDrying^{TR} materials and lower performance of the CS one, mainly in contact with slag.

Field Tests

Castables from the BestDrying^{TR} portfolio has been successfully applied in different steel houses around Brazil, with approved results in the following general scenarios:

Tab. 3: General scenarios of field tests using BestDrying^{TR} refractories in Brazil.

Trough and Runners	Drying Curve Applied	Drying Evaluation	Campaign Performance (In terms of specific consumption)
Slag Runner	0% (eliminated)	Successful	Successful
Pig Iron Runner	0% (eliminated)	Successful	Successful
Main Trough	50%	Successful	Successful
Entire Casting House (including skimmer, tilting runner...)	50%	Successful	Ongoing campaign

In all the tests carried out, the BestDrying^{TR} refractories did not show any anomalies during the drying stage, as well as at the start of operation. During the inspections, the materials showed standard wear, without any point of attention. At the end of the campaign, in all the equipment tested, the BestDrying^{TR} refractories showed wear levels compatible with standard cement-bonded refractory, allowing the maintenance of the specific consumption standards already practiced.

The excellent results collected in the field, as shown in Tab.3, allowed to proceed the next steps, which includes running the casting house after eliminating the drying curve of both the main trough and the secondary runners. In addition, it was possible to calculate the benefits of customers by eliminating the necessity of drying trough and runners in their plants. In a two-main trough blast furnace with a daily production of 7500 tons in which the productivity must be reduced by 10% during the repair period (tap-to-tap operation in only one main trough), 7000 tons of pig iron could be recovered, with a financial return of \$700,000, the non-use of 51.520 Nm³ of natural gas and the non-emission of 100.000 tons of CO₂ into the atmosphere per blast furnace during a full campaign.

CONCLUSIONS

Motivated by the urgent need to increase equipment availability, reduce risk and stress in the casting house, this work aimed to characterize and analyze in the field the new line of monolithic refractories without drying developed by Shinagawa. That was possible by obtaining a binder system with an open microstructure

and without crystalline hydrate that produces a refractory with high permeability and easy water removal. In addition, the novel technology also maintained good workability, mechanical strength, resistance to oxidation and corrosion. In the field, BestDrying^{TR} products are adding up achievements, with slag and pig iron runners operating without any drying and the main troughs already reaching 50% reduction of the drying curve, while maintaining the specific consumption level presented by the line material. Eliminating drying in the main trough is the next step, and the sky as the limit.

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