

REDUCING CO₂ EMISSIONS WITH A ZERO-DRYING CASTABLE FOR BLAST-FURNACE TROUGH AND RUNNERS*

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Abstract

As the steel industry is a major global emitter of greenhouse gases, projects that aim to reduce or eliminate CO₂ emissions within the steelmaking process are urgently needed. In this work, an entirely novel binder system for monolithic refractories, named Fasfrax®, is proposed with the goal of reducing and potentially eliminating the drying step during through and runners repairs. For this purpose, this binder system was studied in an Al₂O₃-SiC-C castable and compared with the two most commonly used commercial binders: calcium aluminate cement (CAC) and colloidal silica (CS). The results showed that the Fasfrax® system successfully produced a 3D gel-like microstructure without the presence of crystalline hydrates. As a consequence, an excellent drying behavior was achieved, even in the most aggressive heating conditions, both in lab and industrial scales, and with no side effects on the high temperature properties. Such positive results highlight that the use of such exclusive binder could lead to the avoidance of up to 500 tons of CO₂ emitted into the atmosphere annually per blast furnace.

Keywords: CO₂ Emission Avoidance; Fasfrax®; Refractories; Drying.

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1 INTRODUCTION

The so-called greenhouse gases have the ability to absorb and re-emit solar radiation, forming the greenhouse layer, a natural effect responsible for maintaining the earth's average temperature suitable for the existence of human life. However, anthropogenic gas emissions enhance this effect by unbalancing the amount of radiation absorbed and emitted by the planet earth, leading to a concerning global warming. So, the primary driver of the current climate changes is the human emissions of greenhouse gases, presenting one of the world's most relevant challenges. [1] Among all greenhouse gases, the carbon dioxide (CO₂) gets most of the attention because it represents about 76% of the greenhouse gas emitted each year and the main share of it, about 62% of the total, comes from burning fossil fuels, including the use of oil, coal and natural gas. For this reason, climate change solutions around the world impose a large focus on reducing the carbon dioxide emissions, mainly for the industrial sector which is the third largest global emitter, being responsible for 21% of the share. As a high-intensive industry, the steel production itself is responsible for one third of all emissions generated by the industrial sector, representing 7% of total CO₂ emitted in the planet.

At the heart of the steel industry are the blast-furnace casting houses, responsible for the reduction of iron ore into pig iron and its subsequent destination for the torpedo cars. The separation of the pig iron and slag generated in the blast furnace takes place in the trough and runners, which are channels on the casting house floor, comprised by metal shells and lined with several layers of refractory materials. The working lining refractories, which are in direct contact with the pig iron and slag at roughly 1550°C, 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 temperature increase during refractories operation results in morphological and volume changes of the unit cell of the hydrated phases generated during reaction of the hydraulic cements. [2] 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 also a large financial loss. In order 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, as shown in Figure 1. When large volumes of castable are applied (general repair) the required drying time reaches 22 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 an average annual consumption of 250.000 Nm³ of this fossil fuel and, consequently, in the emission of approximately 500 tons of CO₂ into the atmosphere (considering a four-tap hole blast furnace with a daily production of 8000 tons of pig iron).

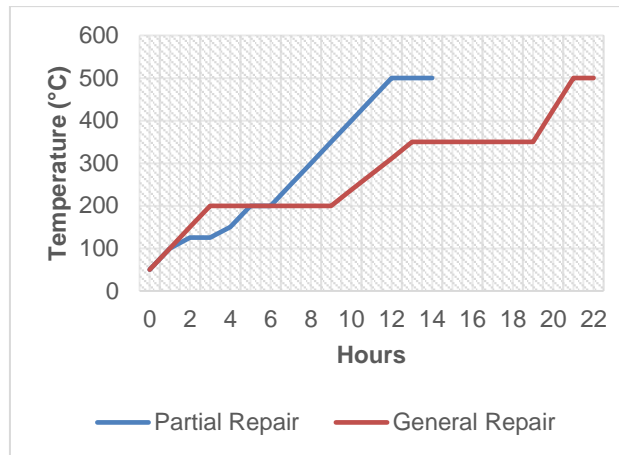


Figure 1. Theoretical drying curve used in through and runners, considering the drying time and temperature for both a partial repair and a general repair. The long plateaus and low heat rate are necessary to avoid accidents during drying.

As an alternative to cement and its inherent drying issues, another type of binder widely used for refractory castables is colloidal silica (CS), formed by an aqueous suspension of amorphous silicon dioxide particles. 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 [3,4]. 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 [3], due to the instability of the colloidal suspension, besides requiring additional transportation costs, as the liquid binder, mostly composed of water, needs to be carried together with the powder mix.

Therefore, the objective of this study was to develop an innovative and high performance binder system (Fastfrax®) 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 CO₂ emission rates.

2 DEVELOPMENT

2.1 Materials and Methods

In order to fulfill the objectives proposed in this work, a standard formulation of through and runners castable (Al₂O₃-SiC-C) was used as the reference for the comparative evaluation of the new proposed system (Fastfrax®) 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 in order to ensure similar levels of flowability for all castables in the study.

Table 1. Formulation of the materials evaluated in this work containing three different binders: calcium aluminate cement (CAC), colloidal silica (CS) and the newly developed Fastfrax®.

| Raw Material (%wt) | Calcium Aluminate Cement (CAC) | Colloidal Silica (CS) | FASTFRAX® |
|--|--------------------------------|-----------------------|-----------|
| Brown Fused Alumina 95% | 56 | 56 | 56 |
| Silicon Carbide | 25 | 25 | 25 |
| Carbon sources | 3 | 3 | 3 |
| CAC 70% Al ₂ O ₃ | 2 | - | - |
| CS 40% solids | - | 10 | - |
| Fastfrax® system | - | - | 2 |
| Others | 14 | 14 | 14 |

2.1.1 Workability

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 applied 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, explosion and corrosion tests.

2.1.2 Permeability

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 (Equation 1) [5]:

$$\frac{\Delta P}{L} = \frac{\mu}{k_1} v_s + \frac{\rho}{k_2} v_s^2 \quad (1)$$

Where ΔP is the pressure gradient of an incompressible fluid of viscosity μ and density ρ flowing through a porous medium of thickness L at velocity v_s , and k_2 is the non-Darcian, or inertial, permeability constant. [5]

2.1.3 Scanning Electron Microscopy (SEM)

In order 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.

2.1.4 Cold Crushing Strength

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. The cold compressive strength test was conducted at Universal Testing Machine KRATOS (model: KE-30.000/E MP).

2.1.5 Fast Drying Tests

For the explosion 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 in order 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.

2.1.6 Oxidation Resistance

Oxidation resistance tests were carried out according to the following procedure: cubic samples of 40mm x 40mm x 40mm were prepared and pre-fired for 3h at 1000°C, in reducing atmosphere. The samples were then placed inside a pre-fired furnace at 1000°C for 6h, under oxidizing atmosphere, so they could go through an aggressive oxidation process. They were withdrawn and, after cooling down, they were cut and the cross-sections were used for measuring the oxidized layer. All formulations were tested together and randomly placed into the furnace to ensure the same temperature conditions and reduce possible deviations generated by the furnace temperature gradient.

2.1.7 Slag and Pig Iron Attack

The corrosion tests were conducted in a rotary furnace heated by torch on samples pre-fired at 400°C. The samples thickness was measured before and after the attack to provide the corroded area of each formulation. For the slag attack, a 70% slag / 30% pig iron mix was used, whereas for the pig iron attack, the mix comprised 80% pig iron and 20% slag. The slag chemical composition is presented at Table 2. The corrosion tests took place for two hours around 1,550°C with the slag and pig iron combination being changed each hour.

Table 2. Chemical composition of the blast-furnace slag used in the corrosion tests.

| SiO ₂ | CaO | Al ₂ O ₃ | Fe ₂ O ₃ | MgO | MnO | Basicity B ₂ |
|------------------|------|--------------------------------|--------------------------------|-----|-----|----------------------------|
| 34 | 45,5 | 10,4 | 0,4 | 5,5 | 0,7 | 1,3 |

2.1.8 Field Tests

The castable containing the novel binder system was also installed at the casting house in a Brazilian steel mill in order to run a pilot trial and confirm the results attained at lab scale. The initial field tests were performed in two 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. Such validation steps were performed in metal and slag runners, in order to ensure that the material would perform well when in contact with both pig iron and slag. A third and final step with 100% reduction of the drying curve was also planned to take place, however it had not been completed until the submission of this article.

2.2 Results and Discussion

Table 3 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 Fastfrax® 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.

Table 3. Water and Colloidal Silica Content, Flowability and Setting Time at 60°C for CAC, CS and Fastfrax® castables.

| Material | Water / Colloidal Sílica Content (%) | Flowability (mm) | Setting Time - 60°C (min) |
|-----------|---|---------------------|------------------------------|
| CAC | 5,6 | 165 | 100 |
| CS | 10 | 154 | 45 |
| FASTFRAX® | 5,6 | 165 | 110 |

CAC and Fastfrax® 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 (k₁) always equal to or less than 0,1.10⁻¹⁴ (Figure 2). As also expected and previously reported [3], 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 k₁ values of the CS material was still not as high as the one attained by the very special structure formed by the Fastfrax® 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.

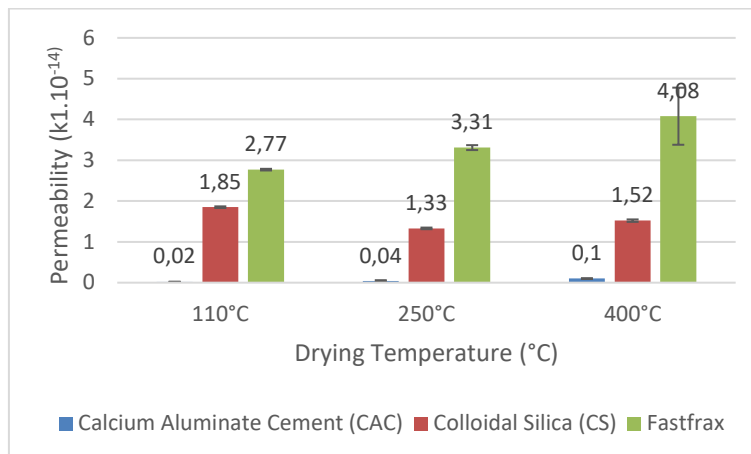


Figure 2. Permeability test comparing the permeability constant k_1 of CAC, CS and Fastfrax® binders treated at different temperatures (110°C, 250°C and 400°C).

In order to better understand the differences in the microstructural evolution of CAC and Fastfrax® during the castable curing step, scanning electron microscopy (SEM) analyses were conducted with samples of both formulations (Figure 3). For the CAC composition (Figure 3.a), it is possible to observe the presence of countless needed 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. [6] When observing the microstructure of the Fastfrax®-bonded castable (3.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.

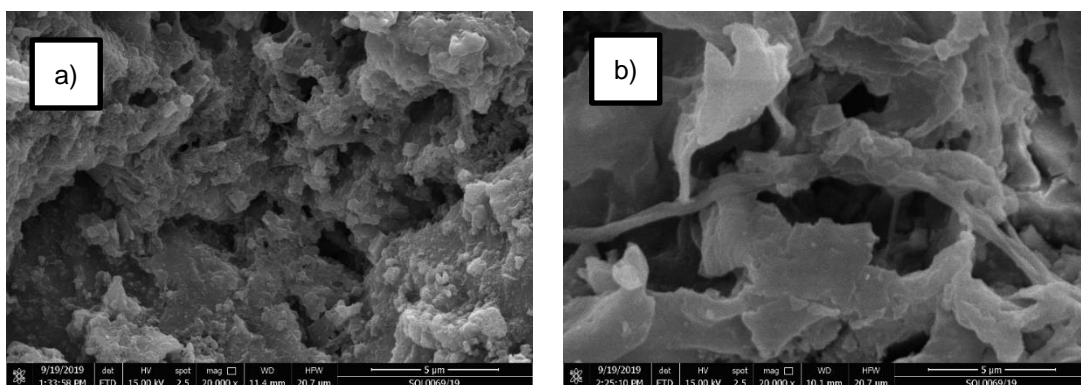


Figure 3. Scanning electron microscopy of the formulation bonded by a) CAC, showing the presence of several needed phases, resulting from the cement hydration process and b) Fastfrax®, with the formation of a gel structure that permeates the entire sample and the absence of crystalline hydrates.

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, 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.

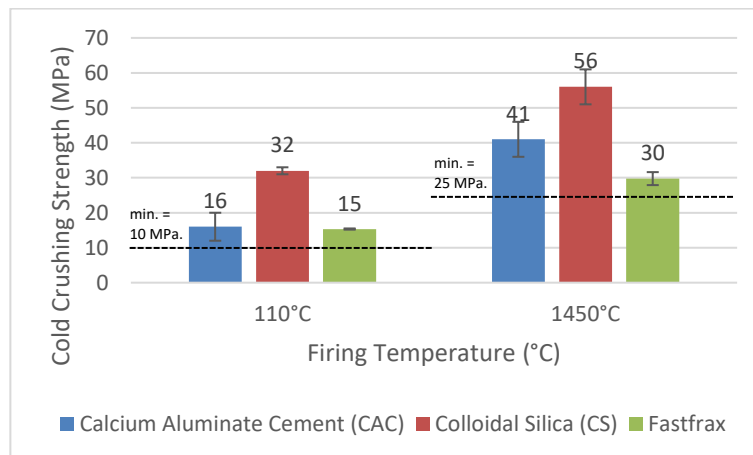







Figure 4. Cold Crushing Strength (MPa) of the castables bonded with CAC, CS and Fastfrax® after dried at 110°C and fired at 1450°C. The minimum values were determined based on historical data.

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 fast drying 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 Fastfrax® material did not present any external or internal damage after the fast drying test. In order to make the test even more aggressive, the curing time of this material was reduced to 8 hours and then 3 hours, and even though the samples still remained intact after testing.

Table 4 Fast drying results presented by the castable bonded by CAC, CS and Fastfrax® after curing at room temperature for different times (24, 8 and 3 hours) and then exposed to 1000°C for 30 minutes. Only the concrete bonded by Fastfrax® resisted all test steps.

| Material | 24 hours curing | 8 hours curing | 3 hours curing |
|-----------|---|--|---|
| | Severely Damaged | | |
| CAC |  | - | - |
| | Damaged | | |
| CS |  | - | - |
| | No damage | No damage | No damage |
| FASTFRAX® |  |  |  |

All pictures were taken after the fast drying test.

After successfully going through all the validation steps in the lab scale, an industrial test was performed for the Fastfrax® 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 Figure 5, indicating that the Fastfrax® binder system proved to be extremely resistant to quick drying procedures, regardless the material volume.



Figure 5. Industrial scale block of approximately half a ton prepared with Fastfrax® 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 Fastfrax®-bonded castable also showed excellent results. Figure 6 depicts the oxidation 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, even with high permeability values, which will allow it to keep good performance during use.

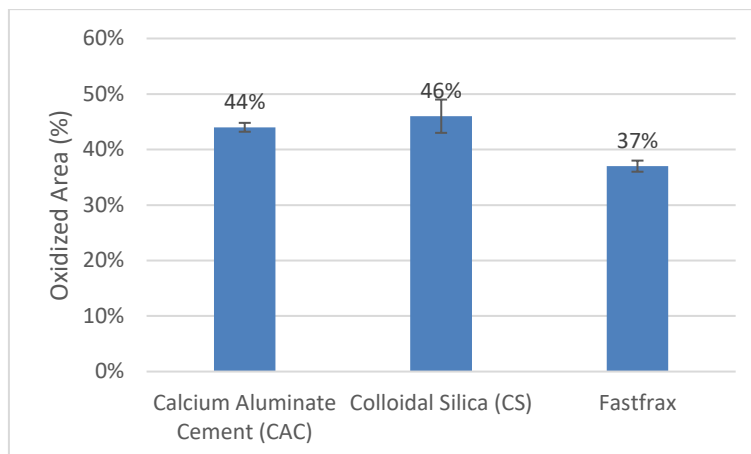


Figure 6. Results of the oxidized area of the evaluated formulations after 6h of exposure to an oxidizing atmosphere at 1000°C.

For the corrosion resistance, Figure 7 shows that the CAC castable performed quite well during both the slag attack and the pig iron attack, whereas the CS composition presented the worst values in both tests. The high chemical stability of the calcium aluminate phases, mainly when in contact with molten pig iron and slag, are well-known and explains its good results. On the other hand, one of the main reported disadvantages of using colloidal silica as a binder in $\text{Al}_2\text{O}_3\text{-SiC-C}$ compositions is its poor corrosion performance when in contact with molten slag. Not only does it promote a more porous castable [4], but in contact with CaO-rich slag, low melting point compounds are formed in the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-CaO}$ system, which help to speed up the liquid infiltration [7]. As a novel solution with a well-deigned structure and no silica addition, the Fastfrax® binder secures a corrosion resistance as high as the one presented by traditional CAC-bonded materials, highlighting the huge potential benefits which could come from the application of such new material at an actual runner.

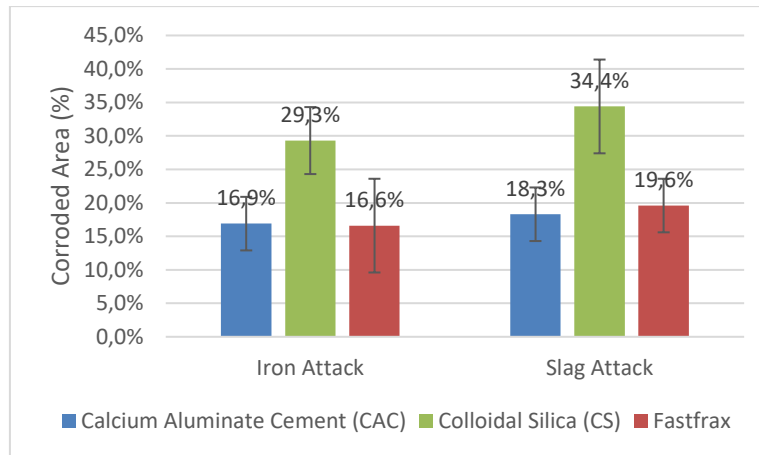


Figure 7. Corrosion tests results of the evaluated formulations at two different situations: pig iron attack and slag attack. Note the similar performance of CAC and Fastfrax® materials and lower performance of the CS one.

For that reason, field tests were performed in a 4-taphole blast furnace with a daily output of 8.000 tons of pig iron. The same $\text{Al}_2\text{O}_3\text{-SiC-C}$ Fastfrax® formulation evaluated in lab scale was applied during the through and runner repair. The installation occurred without any problems, with the castable presenting good flowability and proper setting time. At the first test step, the traditional drying curve was reduced to 50% of its original duration. The drying stage was close monitored and no disturbances were observed. After the end of the campaign, the wear rate of the Fastfrax® material was compared to the wear rate presented by the commonly used CAC-bonded refractory and no differences could be observed. The decrease in the drying curve allowed a consumption reduction of about 10.500 Nm^3 of natural gas, avoiding a monthly emission of 20 tons of CO_2 (Table 5).

After validating this first trial step both at the pig iron and the slag runners, the next phase was performed, reaching 75% reduction in the drying curve. During this campaign, the same results were observed: no issues during the reduced drying step and a good performance of the refractory during operation. With such positive results, it was already possible to reduce 15.750 Nm^3 of natural gas consumption and eliminate the emission of 30 tons of CO_2 per month. The final step of the field trials consisting of an entire elimination of the drying step had not been carried out up to the publication of this article. However, based on the previous results, the estimations are quite positive, with a potential reduction of roughly 500 tons of CO_2 per year in the operation of this blast furnace.

Table 5. Effect of the drying curve reduction on the average natural gas consumption (Nm^3) and CO_2 emission (ton CO_2).

| Data | Regular drying curve | 50% reduction | 75% reduction | 100% reduction |
|---|----------------------|---------------|---------------|----------------|
| Average refractory consumption per month (ton) | 90.000 | 90.000 | 90.000 | 90.000 |
| Average natural gas consumption per month (Nm^3) | 21.000 | 10.500 | 5.250 | 0 |
| Average CO_2 emission per month (ton CO_2) | 40 | 20 | 10 | 0 |

3 CONCLUSION

Motivated by the urgent need to reduce CO₂ emissions in the steel making industry, the present work aimed to develop a novel binder system which could allow the elimination of the refractory castables drying curve. During its curing, the Fastfrax® successfully generated a three-dimensional gel-like microstructure, without the presence of any crystalline hydrates, resulting in extreme levels of permeability. As a consequence, the Fastfrax® castable presented an exclusive easy-to-dry behavior, going through severe laboratory, industrial and field scale testes without any issues. Besides that, the new bonding system provided good workability, oxidation resistance, and chemical stability (in contact with pig iron and slag), highlighting the huge benefits coming from the application of such new material at an actual runner.

In fact, the use of this novel technology allowed a drastic decrease in the drying curve of castables applied at through and runners, reaching a minimum of 75% of reduction. In this scenario the consumption of about 250,000 Nm³ of natural gas was eliminated and a consequent emission avoidance of 500 tons of CO₂ annually was achieved (considering a four-tap hole blast furnace with a daily production of 8000 tons of pig iron). In addition to the carbon footprint reduction in the iron and steel market, Fastfrax® system reduces the downtime of the casting house, enabling an increase in blast furnace productivity.

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