42nd Congress ALAFAR

GRAPHENE-LIKE STRUCTURED TAP HOLE CLAY FOR STABLE BLAST-FURNACE DRAINAGE AND LOWER CO$_2$ EMISSIONS

Deivison Carlos Fontes Hespanhol, Saint-Gobain Performance Ceramics and Refractories, Brazil.
Eric Yoshimitsu Sako, Saint-Gobain Performance Ceramics and Refractories, Brazil.
Heloisa Daltoso Orsolini, Saint-Gobain Performance Ceramics and Refractories, Brazil.
Bianca Maria Gomes da Silva, Saint-Gobain Performance Ceramics and Refractories, Brazil.
Douglas Fernando Galesi, Saint-Gobain Performance Ceramics and Refractories, Brazil.

ABSTRACT

A stable blast-furnace operation is strongly associated with the performance of tap hole clay, which is usually damaged by the combined effect of slag corrosion and pig iron erosion. As such scenario has recently become more challenging due to the use of cheaper raw-materials and low-cost operational practices, Saint-Gobain developed a high-performance solution based on an innovative tap hole clay with a graphene-like structure. Owing to an outstanding chemical resistance and, consequently, a stable mushroom and metal flow, such technology allows operations with reduced fuel consumption, helping to reduce the CO$_2$ emissions and the refractory usage in the ironmaking area.

Keywords: refractories, tap hole clay, blast-furnace, graphene, high performance.

1. INTRODUCTION

The blast-furnace operation is a key step in the steel production chain, as it defines the productivity level of the whole mill. A blast-furnace running with low production level or under unstable conditions will lead to a series of undesired consequences, such as the higher number of torpedo cars out of cycle, an increased demand for steel heating up processes consuming energy, and more important, a lower final product yield. There are many factors disturbing high productivity operation and one of the most concerning ones is the inefficient drainage of metal and slag, which rises the liquid level and causes instability of blast pressure and burden descent

Data citation: Proceeding title and author names available in the first page;

Source: Proceeding 06, XLII ALAFAR Congress, Foz do Iguaçú, Brazil, 2022

[1]. Tap hole clay plays a role of utmost importance in this scenario, as the flow rate of slag and metal being drained out of the furnace is directly related to the degree of erosion of the tap hole area. Kitamura et al[2] and Youn et al[3] evaluated different tap hole clay formulations, pointing out the best combinations for improved corrosion resistance which could, as a consequence, lead to a stable pig iron production.

That means that besides guaranteeing a suitable flow of liquids, the tap hole clay bears also the task of building and keeping a long and robust mushroom in order to better protect the inner walls around the tap hole[4]. Tsuchiya et al[5] conducted a post-mortem analysis of a blast-furnace after the ending of its campaign and concluded that the tap hole length may change depending on the deadman position, which could consequently affect the mushroom stability.

On the top of that, recent cost-reduction practices applied in blast-furnace operations have significantly affected the standard in-furnace conditions, switching towards a circumferential metal flow and a more aggressive slag chemistry[4,6]. Regular tap hole clays available in the market have been struggling to perform well in such an unfavorable condition, mainly because no breakthrough technology has come up in terms of clay formulation in the past twenty years. Standing out from this stagnation process, Sako et al developed in 2017[7] a novel technology based on a suitable plastic behavior and strong adhesiveness, by combining an optimized grain size distribution and an extremely efficient defloculant additive. The main target behind that idea was to supply a tap hole clay which was able, firstly, to fill in properly all the tap hole, without any molten metal infiltration or sealing problems, and then to stick firmly to the hearth wall and to the existing mushroom. Nonetheless, although that was indeed a powerful tool for the hearth walls protection, there was still room for corrosion resistance improvements in order to reach a stable metal production flow.

However, the main common added raw-materials are coke, pitch, tar or carbon black, which are comprised only by amorphous phases and do not tend to graphitize very easily. In other words, they fail in achieving a tough and non-wetting microstructure, which explains the above-mentioned ordinary performance of nowadays tap hole clay.

Thus, in order to complement the state-of-the-art hearth walls protection concept and reach the ultimate tap hole clay technology, this work presents an innovative solution for corrosion resistance based on the development of a graphene-like structure. Graphene is worldwide famous for being the first two-dimensional atomic crystal available, comprised of a sheet of sp2-hybridized carbon[8] and which provides excellent electrical, optical, chemical, thermal and mechanical properties[9]. Due to such attractive compilation of advantages, graphene has been explored as alternatives for electronics, energy-related systems, sensors and many other applications[10]. Therefore, chemical reactions of graphene have a large energy barrier, requiring highly reactive species to initiate the reaction, which makes this structure a perfect alternative for tap hole clay, as its refractoriness is extremely high and it could practically not be corroded by neither slag nor molten metal.

In the present work, by adding a new carbon-containing special additive (CCSA) into a state-of-the art tap hole clay formulation, a graphene-like structure was developed during heating, providing very high mechanical strength (due to very strong carbon bonding) and excellent corrosion behavior, and guaranteeing an ultimate solution for a long lasting protective mushroom.

2. DEVELOPMENT

2.1 Materials and Methods

2.1.1 Formulation

Three compositions were selected to evaluate the formation of the graphene-like structure in the tap hole clay and its benefits. All of them present the same chemical composition, differing only on the additives contents (Table I). A standard formulation was used as the base reference and two new compositions were developed by adding the new carbon-containing special additive (CCSA), in two different concentrations: 0,5% and 1%, hereafter denoted as “THM A and THM B”, respectively.

Table 1. Compositions of the evaluated tap hole clays, with different additives contents.

Raw Materials	**Standard THM**	**CCSA THM A**	**CCSA THM B**
Al_2O_3	20	20	20
SiC	21	21	21
Fe-Si_3N_4	22	22	22
SiO_2+Si	19	19	19
CCSA	0	0.5	1.0
Others	8.0	7.5	7.0

2.1.2 Thermodynamic simulation

The FactSage software was selected to simulate the phase evolution during heating of the tap hole mix with and without the new carbon containing special additive. The calculations of the phases evolution took place at different temperatures: 200ºC, 600°C, 1000°C and 1400°C at reducing atmosphere, using Equilib module. FToxid and Fact53 databases were selected for the calculations.

2.1.3 X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)

To analyze if the graphene-like structure could be formed in actual laboratory conditions, under the influence of reactions kinetic, X-ray diffraction and Scanning Electron Microscopy using EDS (energy dispersive spectroscopy) spotting analysis were conducted. Samples of Standard THM and CCSA THM B were fired, grounded and sieved through the 325 mesh for the X-ray diffraction analyses. The Standard THM sample was fired at 1450°C in order to be used as comparative figure of the existing phases, whereas for the CCSA THM B, the spectrum was obtained for samples fired at 400°C, 800°C, 1000°C and 1450°C in order to analyze in which temperature de graphene-like structure starts to form. Besides that, one sample of THM with the carbon containing special additive fired at 1450°C was polished and covered with gold to be analyzed using SEM technique and EDS. The attained results were compared with thermodynamic simulations to better understand the sequence of reactions and its correlation with the results in laboratory evaluation.

2.1.4 Physical Properties

Prismatic samples (160mm x 40mm x 40mm) were obtained by performing the mixing step according to an internal mixing procedure, followed by uniaxial pressing. After pressing, the samples were fired at 800°C, 1200°C or 1400°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).

2.1.4.1 Hot Modulus of Rupture (HMOR)

The Hot Modulus of Rupture (HMOR) measurements were carried out according to the ASTM C583 standard under three-point bending tests at 800°C, 1200°C and 1400°C. The samples were pressed in a prismatic format (150 mm x 25 mm x 25 mm), pre-fired at their respective test temperature, cooled down, and then reheated during the test, as described in Figure 1.

2.1.4.2 Corrosion tests

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 corrosion resistance index 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 II. The corrosion tests took place for two hours around 1550°C with the slag and pig iron combination changed each hour.

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

SiO2 %	CaO %	Al2O3 %	Fe2O3 %	MgO %	MnO %	Binary Basicity
34	45.5	10.4	0.4	5.5	0.7	1.3

2.1.5 Field Tests

After the lab tests, a pilot trial was conducted in two Brazilian blast furnace (denoted here as BF#A and B), aiming to validate the better performance of the carbon-containing special additive tap hole mix at field conditions.
The blast-furnace #A produces roughly 7000 t, and #B produces roughly 8500 t of pig iron per day.

2.2 RESULTS AND DISCUSSION

Figure 2 shows the thermodynamic simulation for CCSA THM B at reducing atmosphere and different temperatures. The results indicated the likelihood of the graphene-like structure formation in the CCSA THM B formulation even at very low temperatures, pointing out that such structure is thermodynamically stable and, therefore, its presence in the system is very favorable.

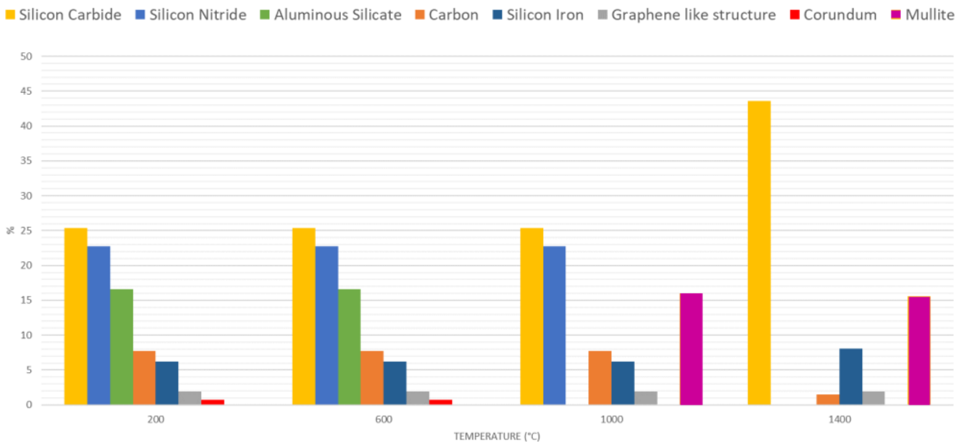

Figure 1. Thermodynamic simulation results for CCSA THM B, pointing out the phases formed at 200°C, 600°C, 1000°C and 1400°C.

Initially, silicon carbide, silicon nitride, aluminous silicate, carbon, silicon and corundum are observed. At 1000 °C, aluminous silicate and corundum phases are not present anymore, giving rise to the formation of mullite. Finally, at 1400°C, an increase in the amount of silicon carbide and a decrease in the amount of free carbon and silicon nitride is observed. It is important to note that the graphene-like structure remains stable at the whole temperature range and that the simulations only considered the thermodynamic barrier for nucleation and growth of a phase. However, when bearing in mind the in situ formation of phases, both the thermodynamic and kinetic barriers must be considered.

Table 3. Description of phases presented at XRD analysis on Figure 3 for Standard THM and CCSA THM B samples.

Formed Phases	**Standard THM**	**CCSA THM B**
Silicon nitride	**Present**	**Present**
Aluminum Oxide	**Present**	**Present**
Silicon Carbide	**Present**	**Present**
Mullite	**Present**	**Present**
Graphite	**Present**	**Present**
Silica	**Present**	**Present**
Iron	**Present**	**Not present**
Graphene-like Structure	**Not present**	**Present**

As seen the presence of graphene-like structure at X-ray, the sample was treated and fired at 1450 °C and analyzed at Scanning Electron Microscopy (SEM). A lamellar structure typical of the graphene one was identified in the tap hole mix with carbon-containing special additive, as described in Figure 2. This is a very relevant result, as it proves that not only was the graphene-like phase formed, as already verified via the XRD technique, but that the phase was surely generated in the unique 2D-structure which guarantees excellent chemical, thermal and mechanical properties. A comparative analyses of properties at laboratory and field scales will be presented in the next section in order to confirm the better performance which could promote a stable blast furnace operation in the steel industry.

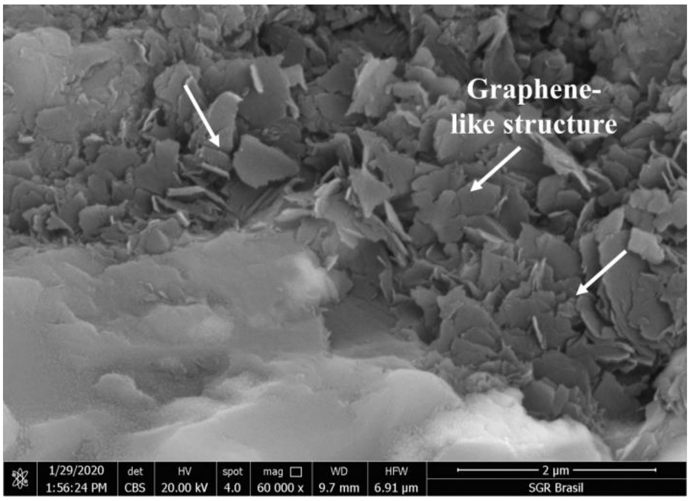

Figure 2. Scanning Electron Microscopy (SEM) image showing the lamellar structure of the graphene-like phase obtained at CCSA THM fired at 1450 °C.

Analyzing the results of apparent porosity combined with cold crushing strength of Standard THM, CCSA THM A and CCSA THM B in Figures 3, it is possible to observe an improvement in the cold crush strength in all temperatures of the formulations containing the special additive.

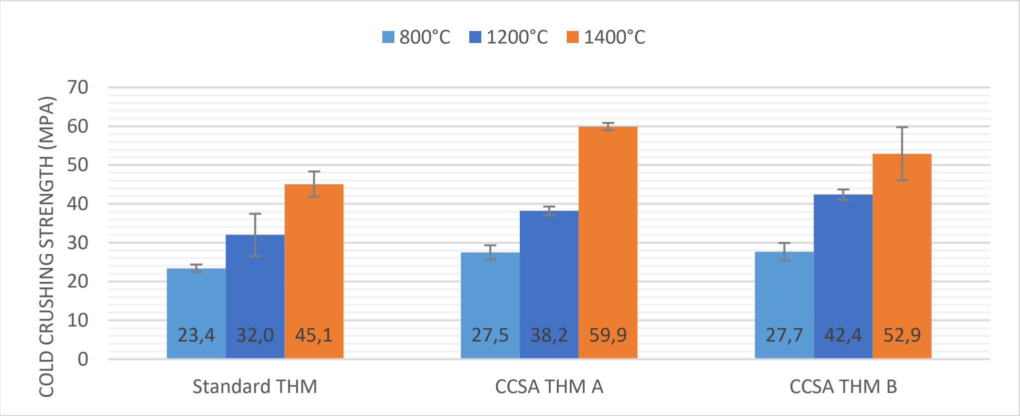

Figure 3. Cold crushing strength (MPa) of the evaluated materials after heat-treatment. at 800°C, 1200°C and 1400°C.

As CCSA THM A and CCSA THM B samples showed an increase in mechanical resistance at the three evaluated temperatures, there was a suspicion of the formation of glassy phase which could lead to higher cold mechanical strength. As the thermodynamic simulation was not enough, because it did not take into account the impurities that are inherent in refractory raw materials and could result in the formation of liquid phases, hot modulus of rupture was measured for the three samples at different temperatures (800°C, 1200°C and 1400°C). From the results present in Figure 4, it is clear that the better mechanical behavior is due to the presence of the graphene-like phase, with no relation to any liquid phase. The CCSA-containing samples showed the highest values of HMOR at the whole temperature range, with CCSA THM B showing the best result of hot mechanical resistance at 1400°C.

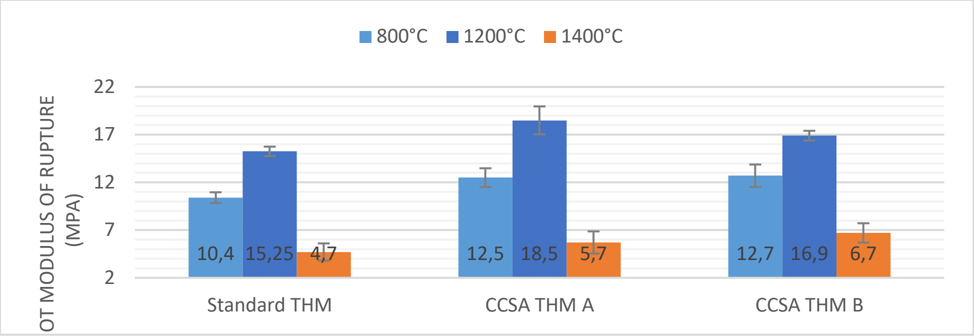

Figure 4. Hot modulus of rupture (MPa) values for “Standard THM”, “CCSA THM A” and “CCSA THM B” samples attained at 800°C, 1,200°C and 1,400°C.

The better hot mechanical behavior, as well as the low wettability features of the graphene-like structure, are favorable aspects for achieving an increased corrosion resistance. Figure 5 presents the wear resistance after slag and pig iron attack in a rotary furnace for the three evaluated compositions, with results being relative to the Standard THM sample. It is straightforward to notice the benefits of the low reactivity of the graphene-like phase, reducing the interaction with both slag and pig iron and, as a consequence, decreasing the wear of CCSA THM A and CCSA THM B samples. In fact, CCSA THM B showed an outstanding performance, with roughly 20% reduction on the slag corrosion, which is directly related to the higher content of the carbon containing special additive present in its formulation.

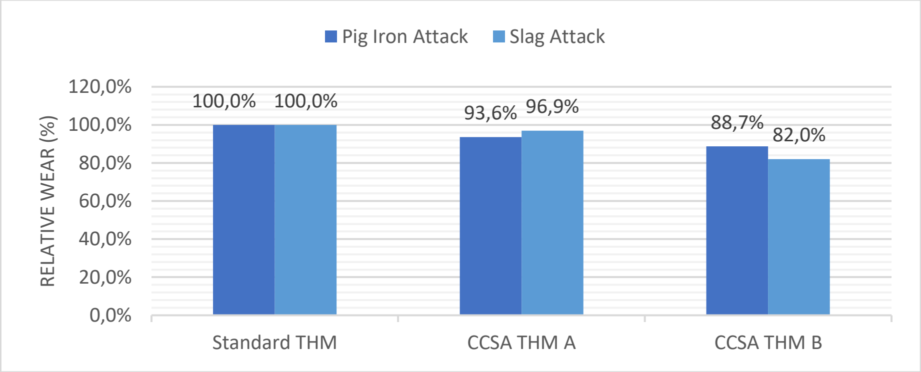

Figure 5. Wear resistance after slag and pig iron attack for the three evaluated compositions. The results are expressed in a relative index, considering the Standard THM as the reference.

The clay followed to field tests after the good results at laboratory tests. At blast furnace “A”, this type of clay with special properties were mainly used at tap hole #1 due its difficulties to achieve higher lengths because of an advanced campaign, closer to maintenance stoppage.

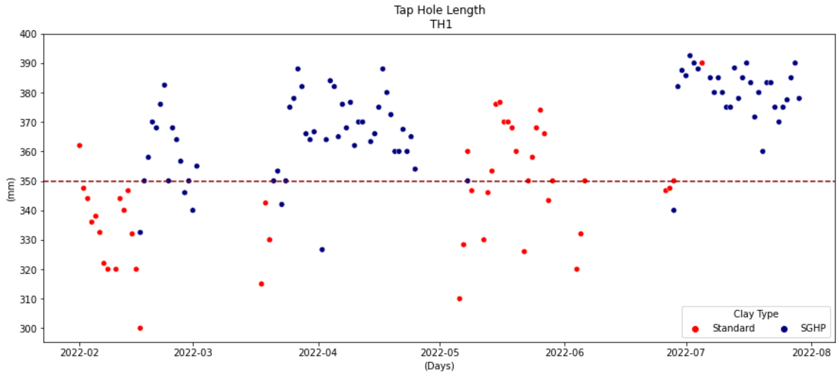

Figure 6. Tap hole length comparing Saint-Gobain High Performance Clay with regular clay over days at blast furnace “A”.

The ability of increasing and maintaining the tap hole length was clearly observed when comparing the results of the regular clay to the new developed high performance tap hole clay, as showed in figure 6. The mushroom stability shows that the area inside the furnace and around the tap hole is well protected.

Analyzing the use at blast furnace “B”, where Saint-Gobain has a higher participation in use of tap hole clay, once can see the stability of tap hole length over the days in a large period of use as shown in figure 7.

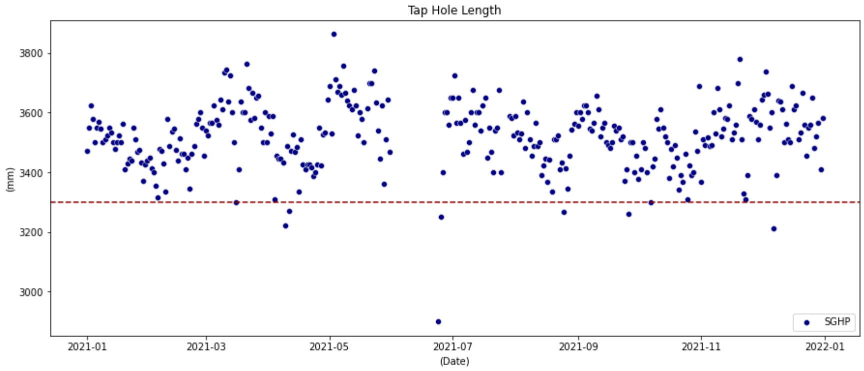

Figure 7. Tap hole length with Saint-Gobain High Performance Clay over days at blast furnace “B”.

Additional to the tap hole length stability, a tendency of coke rate decreasing is presented in figure 8. As coke is the main fuel of blast furnace, the result is related to less carbon loaded at the furnace.

This relation is not easy and simple to make, the conditions of operation of furnace was quite complicated last months due global economic condition. Even though, the results have indicated a positive effect of an engineered and high performance refractory on a safe and sustainable operation of blast-furnaces.

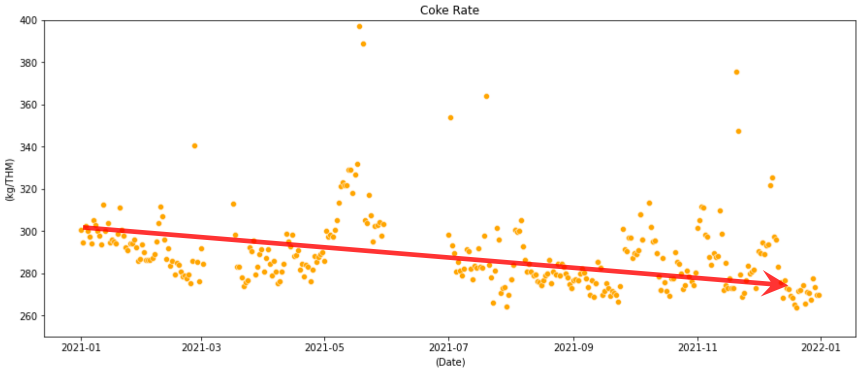

Figure 8. Coke rate at blast furnace “B” over days.

3. CONCLUSION

An ultimate tap hole clay technology was presented in this work, based on the introduction of a graphene-like structure by adding a carbon containing special additive, which was able to provide excellent chemical, thermal and mechanical properties. Thermodynamic calculations and microstructural analyses showed the stability of such phase in the tap hole clay structure, whereas laboratory tests confirmed its main benefits: higher mechanical strength and enhanced corrosion resistance.

The field tests in 2 different blast-furnaces with large production pointed out that the excellent properties of the novel tap hole clay observed in the laboratory were responsible for making the furnace operate with stable tap hole length which is related with stable drainability and hearth protection. A better protection of the hearth walls could also be observed, consequently reduce consumption of clay, less use of raw materials to produce clay and possibility of decreasing use of fuel loaded at furnace, in other words less carbon used.

Both results evidenced the breakthrough advance brought by this novel technology, which was able to keep high performance even during the current scenario of constant changing of operational conditions.

4. REFERENCES

1 Nouchi T, Sato M, Takeda K, Ariyama T. Effect of operation condition and casting strategy on drainage efficiency of the blast-furnace hearth. ISIJ International. 2005; 45(10): 1515-1520.

2 Kitamura M, Nakamura R, H. Sumimura H. Study of the high density tap hole clay for blast furnace. Journal of the Technical Association of Refractories. 2002; 22(4): 350-354.

3 Youn S, Kim K, Choi M. Development and application of high Al_2O_3 tap hole clays for

blast-furnace. Unitecr 97 Proceedings. 1997; 97: 693-704.

4 Spaleck K, Schoeman M, Seegers W, et al. Practices and design for extending the hearth life in the Mittal Steel Company blast furnaces. Fifth European Coke and Ironmaking Congress. 2005; 5: 10-15.

5 Tsuchiya N, Fukutake T, Yamauchi Y, Matsumoto T. In-furnace conditions as prerequisites for proper use and design of mud to control blast-furnace tap hole length. ISIJ International. 1998; 38(2): 116-125.

6 Laar RJ, et al. Blast furnace hearth management for safe and long campaigns. Iron and Steelmaking Technology Conference Proc. 2003; 1079–1090.

7 Sako EY, et al. High performance taphole clay: a key for blast furnace hearth protection and a tool for cost reduction. Iron and Steel technology. 2018; 82-87.

8 Novoselov KS, Falko VI, Colombo L, Gellert PR, Schwab MG, Kim K. A roadmap for graphene. Nature Research 2012; 490(11): 192-200.

9 Allen MJ, Tung VC, Kaner RB. Honeycomb carbon: a review of graphene. Chemical Reviews. 2010; 110(1): 312-145.

10 Rana K, Singh J, Ahn J. A graphene-based transparent electrode for use in flexible optoelectronic devices. Journal of Materials Chemistry C. 2014; (2): 2646-2656.