Low phenol binding system for high performance environmental friendly Taphole Clay

A. MOUSTAPHA*[1], Steffen MOEHMEL[2] Pascal HUBERT[3]

[1] Science & Technology Engineer, *Calderys Deutschland, Neuwied*
[2] Senior Science & Technology Engineer, *Imerys ITCA, Villach*
[3] Senior Science & Technology Engineer, *Imerys ITCA, Villach*

Abstract

The new climate and environmental challenges have made the iron-making industry move towards cleaner production and therefore to greener refractory consumption. The blast furnace is the main vessel in the iron-making process, its tapping mainly relies on the quality of the Tap-hole Clay (THC). For a long time, coal tar-bonded THCs were used for their easy injection and good adhesion to the taphole walls but their high toxicity led to the use of phenolic resins. Despite their lower toxicity level, these resins are recently presenting some health issues for the plant workers, especially with their free phenol content which sometimes can be present up to 10% in the resins. This study examined and compared two different resin binding systems: a conventional phenolic resin and a low free phenol resin. On the first hand, the effects of these binding systems on the general plastic behavior of the products were analyzed and also correlated to their physical and mechanical properties. A comprehensive understanding of the taphole's severe operating conditions such as high temperature, high pressure, and corrosion by slag and molten pig iron is required. Therefore, the injectability of the studied samples was investigated at high temperatures to characterize the setting of the material, the cracks formation, and the outlet of volatiles during the plugging mechanism of the THC in the blast furnace. A chemical analysis of the Polycyclic Aromatic Hydrocarbons (PAHs) present in the samples was also performed.

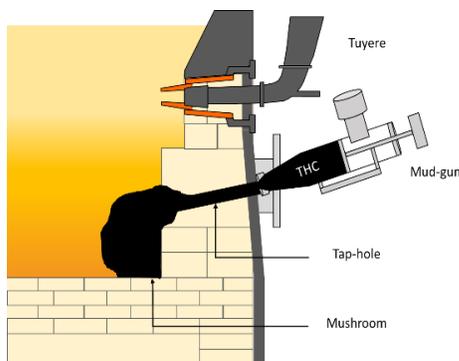**Keywords:** THC, Blast Furnace, PAHs, Taphole, Plugging, Low phenol, Resin

Fig. 1.Cross-section of the Blast Furnace (BF) Taphole area

1. Introduction

The blast furnace (BF) is a complex pressure reaction furnace used to melt iron ore. Being the best and most efficient route possible for the iron-making process, the productivity of the blast furnace is a major point of consideration. The taphole is located at the bottom part of the furnace and is used to drain out the liquid iron resulting from the reduction process. Depending on their size and capacity, BFs can have multiple tapholes to assure constant and high productivity. Using a pressure piston tool called "mud gun", the tapholes are filled with a special plastic refractory commonly known as Taphole Clay (THC) that seals and assures hermetic closure of the holes during melting. The injected product will solidify while releasing the volatiles inside and expand to form a long pipe covering the whole taphole. During the plugging, a protective layer also called "mushroom" is formed and will protect the refractory lining of the BF as shown in **Fig.1**. The high temperature gradient, high pressure, frequent drilling, and plugging expose THCs to an extremely

dynamic environment. Therefore, a high-performance material should have a controlled plastic behavior to be easily introduced in the hole, an adequate setting time to allow the volatiles to evenly escape the structure and a strong resistance to chemical attack by slag and mechanical wear from the molten iron flow.

Phenol formaldehyde resins also known as phenolic resins belong to the synthetic polymers family and are obtained by the reaction of the phenol with the formaldehyde. THC with phenolic resins as binders generally involves two types which are Novolac and resol. These resins will either act as a thermoplastic (Novolac) or thermosetting (Resol), depending on the ratio of formaldehyde to phenol. Both of these resins will have an important concentration of unreacted phenol (2-15%) which is referred to hereinafter as free phenol [1].

Different studies on environmentally friendly THC have assessed the property differences and changes between coal tar THC and phenol resin bonded THC [2]. But the constant changes in regulations and customers' requirements lead to a permanent improvement of the products. Nevertheless, recently the toxicity level of the free-phenol content in phenolic resins had caused some health issues.

In this study, a new resin containing less than 1% free phenol was applied and compared to the currently used resin with more than 10% free phenol.

2. Experimental Procedure

Raw Materials and samples composition

Typical THC composition consists of Al-SiO2-SiC-C materials. The aggregates part is mostly dominated by coarse alumina grains, Yoshimura et al [4] have proven that the choice of the alumina aggregates composition and amount in THC can have a strong impact on corrosion resistance. On the other hand, the matrix is generally composed of fine Alumina, SiC, and carbon which enable resistance against erosion, and oxidation but also allow the release of volatiles by judicious packing and choice of grain sizes. Other additives such as Fe-Si3N4 are mostly used for corrosion resistance.

Finally, the binders which are usually referred to as the liquid part of the composition will hold and coat the particles to procure the material the required plasticity, high strength behavior, and cohesiveness. This will have an impact on the extrusion properties of THC but also on the setting time. Coal tar and pitch are by far the most used binders in THCs [3] for their high performances, especially for the good plasticity they supply to the products. Phenolic resins compared to coal tar and pitch have low thermal stability and can solidify prematurely causing a shortening of the taphole length but can also strick and solidify in the mud gun on itself making further plugging difficult and almost impossible. After the plugging and the release of volatiles, carbon contained in the remaining liquids will help the structure of the material to strengthen by increasing the high temperatures performances.

Tab.1 summarizes the composition of the studied THCs. Resin A is the conventional one with a free-phenol content above 10% while resin B is the newly developed binder with a free-phenol content below 1%.

Composition (%)	THC A	THC B
Al_2O_3	37	37
SiC + C	33	33
SiO_2	16	16
Others	14	14
Binders	Resin A	Resin B
Free-phenol	12	0.4

Tab. 1. Compositions of the studied THCs
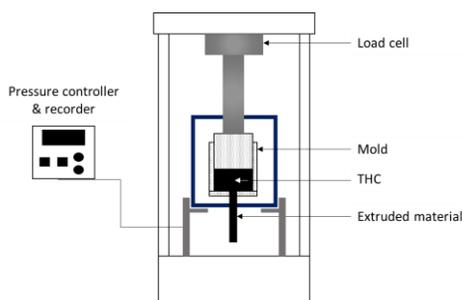
Test Methods

Fig. 2. Extrusion resistance apparatus (Marshall test)

The plasticity of the THC was tested according to the Marshall method where a sample is pre-heated at 3 different temperatures of 35, 70, and 135°C and placed into a mold to be pressed out with a 0.57 mm.s-1 speed. The given value by the apparatus shown in **Fig. 2** corresponds to the maximum load needed to extrude the material.

The used resins, as well as the THC mixes, were chemically analyzed using gas chromatography and mass spectrometry. The aim here was to investigate the Polycyclic Aromatic Hydrocarbons (PAHs) contained in the materials to compare them.

Both THCs' mechanical and physical properties were also assessed at 800°C and 1500°C. The Cold Crushing Strength (CCS) was evaluated using a mechanical press. Depending on the type of BF, the working environment can be very hostile for THC due to the dynamic molten iron flow. Therefore, favoring slightly higher CCS values allow the products to withstand crumbling and thus avoid a liquid penetration that could lead to a self-opening of the taphole. However, a high-quality THC should also be easy to drill and consequently, a very high CCS is not favorable. The Permanent Linear Change (PLC) was also measured to evaluate the capacity of THC to expand or shrink during heating. The bulk density (BD) and apparent porosity (AP) were measured according to the standard Archimedes method with water immersion [DIN EN 993-1].

The hardening time, also known as the "setting time", is a major property of THC. In fact, the gradually increasing temperature in the taphole will bring the material to a hardened structure in a short or long period of time. To trace the setting time, the studied THCs were heat treated at 300°C for different time intervals and then mechanically loaded to measure the sagging rate. The polymerization of the used resins usually starts between 90°C and 130°C but depending on the kinetic of the reaction, the polymerization may differ. A rapid cold quenching was performed to stop the reaction and thus evaluate the hardening process of the samples.

A plugging simulator developed at a lab scale was used to simulate the plugging mechanism of the product in a taphole. Using a piston press, the material was plugged into a glass tube at 1050°C. The injection pressure and the temperature gradient were also measured. **Fig. 3** illustrates the testing mechanism.
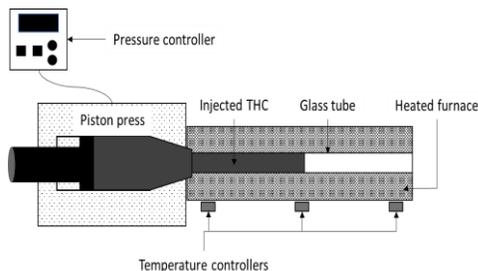

Fig. 3. Schematic representation of the plugging simulator

3. Results and Discussion

THC extrusion resistance and setting behavior

The plasticity of THC tends to increase when the liquid amount in the formulations increases ie. a low extrusion resistance (ER) behavior for THCs means an easy injection in the taphole and a better gap filling [5]. In this study, the dry raw materials content remained unchanged to see the real effect of the new resin on a chosen THC formulation.
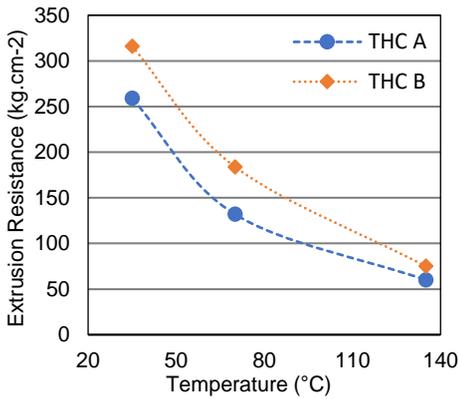
Fig. 4. Extrusion resistance at different temperatures

Fig. 4 shows the results of the extrusion test for THC A and THC B. The sample with the newly developed resin has slightly higher values of ER for low temperatures and almost similar values are observable at 135°C. Therefore, a low free-phenol resin will not have an impact on the plasticity of THC. High-quality THC is a material that properly sticks to the tap-hole walls and can smoothly adhere to the previous THC. The injection of the product into the hole is a delicate process influenced by several parameters specific to the BF operation such as the temperature, the internal pressure, and the type of mud gun used [6]. But it can also be influenced by parameters directly related to the quality of the THC such as its expansion behavior or even its setting time. In fact, a material that rapidly sets will not have the time to fill the entire hole and will give room to some cavities where the molten iron and slag can penetrate. and will sub consequently cause unrecovered weak mushroom. The phenomenon of "self-opening" can therefore occur and have tremendous consequences on the productivity of the BF if coupled with low corrosion resistance properties. **Fig. 5** shows the sagging rate of the studied samples after heat treatment for 1, 5, 10, 15, 20, and 30 min. It is observable that the sagging rate of the conventional THC A is dropping rapidly and finally starts to harden after

10 min whereas the setting process of the new THC B is more homogeneous with a hardening time above 15 min.
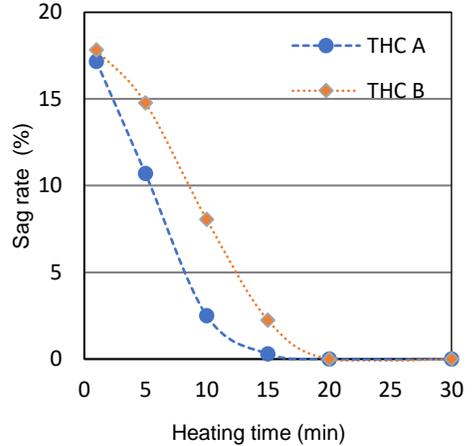

Fig. 5. Sagging rate of the materials at 300°C for different time

Mechanical and Physical properties

The CCS and BD, OP, and PLC of the studied samples are shown in **Fig. 6** and **Tab. 2** respectively. Higher CCS is observable for the new resin (THC B) at 800°C and 1500°C. The BD is quite similar for both materials but the results showed slightly higher values for the new development. BD and CCS can sometimes be correlated as a high density material has a higher CCS. The difference at 1500°C here is clearly coming from the resin source where the new resin has a better bonding mechanism at higher temperatures. The porosity of THCs is also linked with the mechanical strengh as pores facilitate the crack propagation with their stress concentration effect. Here also, the samples are presenting a diffirence in OP, a decrease of almost 19% is noticeable between THC A and THC B with the new binder. Different PLCs can generally be observed when varying types and quantities of raw materials are used. As already mentioned, for the investigated THCs no changes have
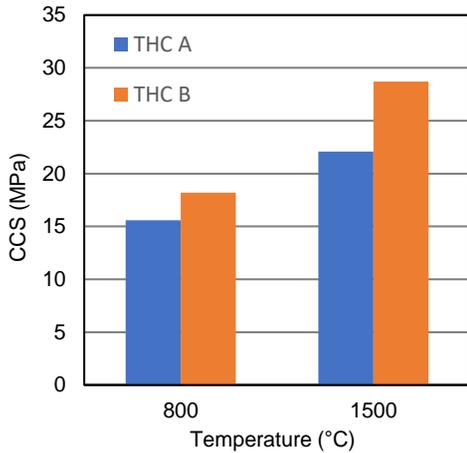
Fig. 6. Cold Crushing Strength at 800°C and 1500°C

Properties		THC A	THC B
800°C			
Bulk density (BD)	g.cm-1	2.2	2.2
Open Porosity (OP)	%	22	18
Post Linear Change (PLC)	%	-0.5	-0.3
1500°C			
Bulk density (BD)	g.cm-1	2.2	2.2
Open Porosity (OP)	%	23	19
Post Linear Change (PLC)	%	-0.7	-0.4

Tab. 2. Physical properties at 800°C and 1500°C

been made except for the liquid part. For both materials, a similar PLC below 1% is observable at 800°C. A significant difference occurs after treatment at 1500°C where THC A continues to shrink while THC B stayed constant. Therefore, the new development will have a stronger tap-hole filling behavior than the conventional material.

THC toxicity level: PAHs

PAHs are classified on their harmful effect and on a CMR (carcinogenic, mutagenic, reprotoxic) scale. The most known PAH is benzo[a]pyrene (BaP) which is highly classified as carcinogenic. The European Union's REACH Regulations (Registration, Evaluation,

Substances	Limits (ppm)	RPF
Benz[a]anthracene	1000	0.033
Chrysene	1000	0.26
Benz[e]acephenanthrylene	1000	0.1
Benzo(k)fluoranthene	1000	0.01
Benzo[a]pyrene	100	1
Indeno[1,2,3-cd] pyrene	10000	0.1
Dibenz[a,h]anthracene	100	1.4
Benzo[ghi]perylene	-	1

Tab. 3. REACH limitis for BaP group and RPF

Authorization, and restriction of CHemicals) constantly update the limits for the PAHs and BaPs, the latest limits are shown in **Tab. 3**. In THCs, the only

Substances	Resin A	Resin B	THC A	THC B
Phenol	1600	347	448	63
Formaldehyde	75	135	1	9
PAH				
Naphthalene	11700	5	17	0
Acenaphthylene	100	1	8	0
Acenaphthene	21500	1	1	0
Fluorene	18500	5	12	1
Phenanthrene	18600	15	37	1
Anthracene	2050	1	7	0
Fluoranthene	5930	20	2	2
Pyrene	3430	56	2	0
Benz[a]anthracene	118	1	3	0
Chrysene	88	2	1	0
Benz[e]acephenanthrylene	42	3	0	0
Benzo(k)fluoranthene	41	2	0	0
Benzo[a]pyrene	56	6	5	0
Indeno[1,2,3-cd]pyrene	130	10	2	1
Dibenz[a,h]anthracene	3	0	0	0
Benzo[ghi]perylene	134	33	1	1
Toxicity level	238	41	7	1

Tab. 4. PAH of tested resins and THCs and their toxicity level

source of PAHs is the phenolic resins or even coal tar and pitch which have a high toxicity level and are not used in Europe. With the high temperatures and pressures in the tap-hole and with their low melting point, these substances can get out of the THC and lead to the formation of aerosols that would cause chronic poisoning. **Tab. 4** shows the PAHs gas chromatography analysis of the resins A and B as well as the finished products THC A and THC B. A clear difference between resin A, with a phenol content of 1600 ppm in comparison to a low amount of 347 ppm for the new resin B can be observed. The same observation is made for the final product THC A and THC B where only 63 ppm of phenol is contained in the new development. RPF which is the Relative

Potency Factor is generally used to calculate the toxicity level of some products based on their PAHs content and especially on the BaP. In fact, according to their group and their carcinogenic behavior, RPF can be calculated (stated values in the literature [7]), and thus the toxicity level by the sum product of RPF and the sum of PAHs. As shown in **Tab. 4** THC A is more toxic than THC B which is confirmed by the results of the resins' toxicity.

Plugging simulation test

The plugging simulator was thought and engineered in order to assess the quality of our THCs while trying to create an environment that is as close as possible to real working conditions. **Fig.7** shows the outlet part of the injected material for THC A and B. These samples were cooled at room temperature for 24h after the test and as one can observe, THC A shows different segmented small parts. This is mostly due to the unmolding of the sample from the glass tube. In fact, the transversal cracks which had formed during the test weakened the material and brought it to its breaking. On the other hand, THC B is showing a smoother external texture with fewer longitudinal cracks. These observations can be directly correlated to the setting behavior of both samples. In fact, as previously seen, conventional resin A tends to procure a fast hardening and precipitates the release of the volatiles in unfavorable directions and therefore initiates an uneven transversal cracks formation. As some volatiles can still remain in the structure of the material as well as for a complete understanding of the mechanism the volatiles matters were calculated before and after the test. Samples from THC A and THC B were fired at 1000°C in order to get the total volatiles release before the test. The same procedure was undertaken with samples after the plugging test. The results for the loss on ignition are shown in **Fig. 8**. As can be observed, a higher amount of volatiles was still remaining in
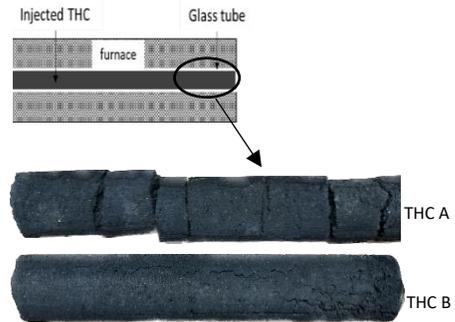

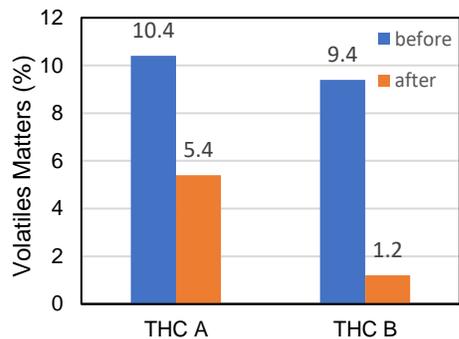**Fig. 7**. Surface texture and cracks appearance after the test

Fig. 8. Volatiles Matters before and after the test

THC A compared to the total amount. Only 5 % could escape from material A, which represents half of the total amount whereas, for THC B, all gases could almost find their way out. It is important to bear in mind that the samples were injected directly in a heated furnace at 1000°C. The appearance and the cracks overview can inform on the ability of both materials to withstand rapid heating and thermal shock.

Conclusions

The new low phenol and low toxicity binding system showed high and promising performances. By lowering the amount of PAHs in the resin, the toxicity level of the final THC product could drastically decrease. And enhancement in the general properties as well as the high temperatures properties could be observed. The correlation between the porosity and the mechanical strength has allowed to clearly place resin B as a

stronger bonding agent compared to the conventional resin. Using a plugging simulator, the injectability on the studied THCs could be investigated and correlated to their setting behavior and the volatiles release but also to the crack's initial formation and propagation direction. A smoother volatiles release resulted for the new development favorited by longitudinal cracks with a homogeneous setting throughout the time. A low phenol, low toxic with higher mechanical and physical properties material was developed and assessed at the customer proving that the move towards greener refractories and TapHole Clay is possible and achievable while enhancing performances.

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