Optimal Refractory Solutions for Natural Gas-Hydrogen DRI Reactors

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ABSTRACT

Direct reduction of iron technologies has proven to have lower CO_2 footprint compared to the conventional blast furnace routes and are further moving towards higher hydrogen content in the reducing gas in order to minimize the direct CO_2 emissions. High hydrogen concentration in the reducing gas may react with the refractory and change its text physico-chemical characteristics, resulting in an alteration of chemical and mechanical resistance as well as a change of the thermal gradient in the refractory lining. This paper reviews the functional requirements of the refractory linings of a DRI reactor with higher percentage of H_2 in the reducing gas and recommends optimum total solution, brick, monolithic and jointing products, based on the past experience and recent experimental studies.

Keywords: Refractory, Green Steel, DRI, Bricks, Castable

INTRODUCTION

The steel industry contributes to 8% of the global CO_2 emission as per the International Energy Agency [1]. The majority part of the global steel production is via the blast furnace–basic oxygen furnace (BF-BOF) route [2]. The blast furnace ironmaking process uses coke, pulverized coal to reduce iron oxide is the predominant primary metal production process and emits approximately 70% of the total CO2 emission of the entire steelmaking route [2]. Hence, the blast furnace route is under pressure to reduce carbon emissions particularly in Europe as the CO_2 footprint reduction is getting more and more attention. Three different strategies are now considered as a solution towards carbon footprint reduction. They are BF-BOF routes coupled with carbon capture utilization / storage (CCU/S), electric arc furnace (EAF) scrap melting and refining and direct reduction of iron (DRI) using hydrogen. The first two processes have their own limitations. However, the DRI technology is fully established and operating under CO and H2 environments where H2 can be as high as 75 %. The process can be further modified to operate under 100% hydrogen concentration, thereby reducing CO_2 emission between 100 and 400 kg/t steel to reach the net zero at 2050 [3].

DRI Technologies and Process Conditions

Most of the DRI plants operate under natural gas (NG) and further melt the DRI in an EAF. The DR-EAF route significantly decreases the consumption of coke and coal but still results in some carbon emissions owing to the use of NG. In order to make the ironmaking process carbon neutral under the NG must be replaced by green hydrogen. The two main technologies of the DRI already in use are MIDREX and HYL/ENERGIRON. The inlet gas temperature and pressure can be as high as 950°C and 1.5 bar for MIDREX whereas 1150 °C up to 8 bar for HYL. The maximum hydrogen to carbon monoxide ratio can be as high as 75%. Both MIDREX and HYL are developing processes capable of using 100 % hydrogen in the inlet gas [4, 5]. These processes with increased hydrogen partial pressures demand special refractory materials.
Calderys has successfully designed and developed complete refractory solutions for the DRI process.

Refractory Design Considerations

Under the H_2 and CO conditions there are two main concerns for the refractory i.e hydrogen attack of silica and CO attack on iron containing impurities. As the hydrogen partial pressure increases at high temperature, it dissolves silica (SiO_2) in the refractory brick [6]. The high diffusivity of hydrogen further helps the reaction (1) in the forward direction, further weakening the brick strength.

$$H_2(g) + SiO_2(s) \rightarrow SiO(g) + H_2O(g) \quad (1)$$

The reaction kinetics depends on the temperature, the H_2 concentration in the gas phase and SiO_2 concentration in the solids [6]. It has been reported that silica glass dissolves faster than mullite [6]. As per Crowleyh [7] the total pressure and presence of water vapor tend to slow down the reaction.
The possible CO attack of refractories containing iron impurities is a well-known phenomenon. There has been no evidence in the literature about the combined attack of CO and H_2 to our knowledge.
The high diffusivity of hydrogen in the refractory destabilizes thermal profile in the linings and hence the dew point position. This must be taken into consideration to avoid dew points, consequently leading to gas condensation and increased corrosion [8].

EXPERIMENTAL SET-UP & TESTING

Seven different brick products containing various types of aggregates and alumina content along with a dense tabular alumina castable (sample I) and an insulating lightweight castable (sample J) were also included in the study. Details of the selected samples are summarized in table 1.

Corrosion test

The samples were placed in a furnace with a controlled atmosphere containing 25% of CO and 75% of H_2 under 2 bars absolute pressure at two temperatures. At 630°C four heating cycles were performed, in each cycle, the temperature was maintained for 50, 70, 60 and 60 hours successively. At 930°C, 3 cycles, each of 80 hours were applied. The total exposure time of the samples to the gas composition was therefore 240 hours in both cases. Sample inspection and measurements were carried out at the end of each cycle. These temperature conditions were determined based on the Boudouard reaction and process temperature of the DRI process.

As there is no standard procedure to assess the resistance of refractory materials under H_2 & CO atmosphere, it was decided in this study to proceed as follows:

- between each cycle, the Young's modulus E was evaluated by resonant frequency,
- weight variations were measured.
- visual inspections of the samples were also performed to highlight possible carbon growth.

The visual assessment rule for CO resistance of the refractories was carried out as per the ASTM C 288 standard.

	Alumina [%]	**Aggregates**
A	85	Bauxite* (* Phosphatic binder)
B	42	Low Iron Fireclay
C	45	Low Iron Fireclay
D	75	Mullite
E	92	Corundum-Fused Mullite
F	95	Corundum
G	99	Corundum
I	95	Castable Tabular Alumina
J	42	Lightweight castable Fireclay

Table 1: alumina content and main aggregate type in the samples of the study

RESULTS AND DISCUSSION

Young's modulus, E

The evolution of Young's modulus E of various samples after 240 hours under the test condition for two different temperature conditions is shown in Fig. 1. Young's modulus was measured at each break. It was observed that the decrease in E was highest after 50 hours and stabilized afterwards. Bauxite based material showed a significant drop in Young's modulus after 240 hours

of testing at 630°C. It may be linked to the iron content of this material as they react under CO condition [8].
The castable samples were only tested at 930° C. The dense tabular alumina castable showed a larger reduction of Young's modulus than the other samples compared to the lightweight castable (sample J).

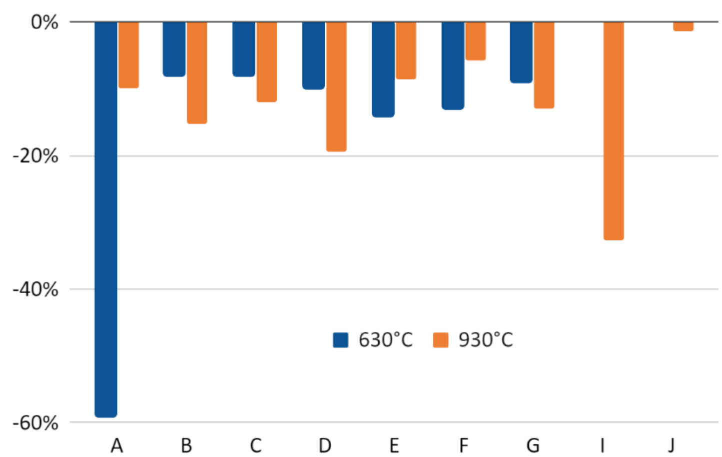

Fig. 1 Evolution of Young's modulus at the end of 240 hours

Corrosion

The corrosion of the samples was evaluated by measuring the weight loss of each at the regular interval. These results are shown in Fig. 2 and Fig. 3 below. Though the corrosion of the refractory was quite moderate, it was observed that the corrosion was more at higher temperature. It was also observed that high alumina samples showed less corrosion compared to others as given in the literature [8]. Bauxite brick was showing the highest corrosion among the brick samples despite having a quite high Al_2O_3 level.
The castable samples showed higher corrosion compared to brick samples though having similar amounts of Al_2O_3. Insulating castable, showed highest corrosion probably due to the high porosities of the sample exposing larger surface area of interaction with the gas phase.

Carbon growth

Carbon growth of the samples was assessed on regular intervals through visual inspection. Bauxite based bricks were observed to have been worst affected showing carbon growth after 240 hours under 630°C. It was observed that few samples were damaged and were partially broken at the end of the testing under 930°C. Boudouard reaction is favored by iron impurities and the observed carbon growth can be correlated to the presence of iron impurities in the aggregates [8]. Two samples out of 42 tested found to have small black spots or black coloration after 50 hours at 630°C on the fireclay materials. But, there was no evolution of these black spots with the duration of the test.

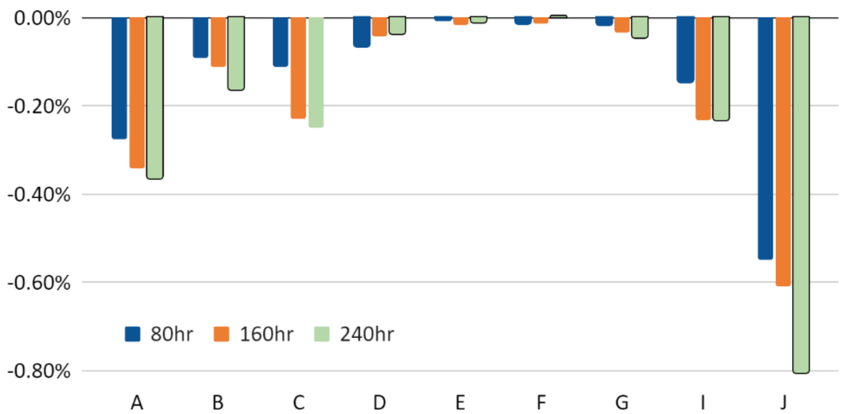

Fig. 2 Weight loss of sample A to J at 930°C

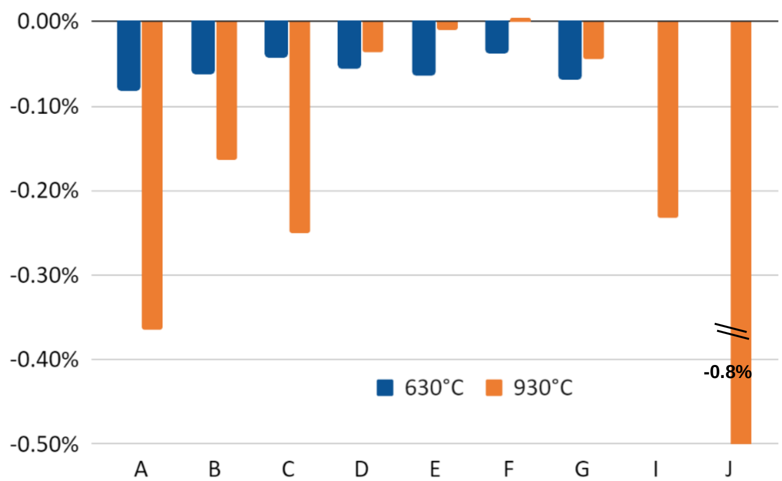

Fig. 3 Weight loss of samples A to J at 630 and 930° C after 240 hours

CONCLUSION

This article demonstrates the process of refractory product development through combined literature and experimental studies. This does not include the vast numerical simulations work we carried out. The experimental works were designed to simulate as closely as possible the simultaneous influence of hydrogen, carbon monoxide and temperature conditions prevailing in a DRI kiln on the refractory lining. High alumina dense bricks are found to be the best materials under DRI conditions at higher temperatures. Castable, with a high total alumina content, do not seem to be as resistant as bricks. Further studies are undergoing to understand the mechanisms and to design appropriate castable microstructure. Present studies, extensive simulation work (not part of this article), DRI process know-how and the past experience has enabled us in developing complete refractory solutions for the green steel. We will continue to monitor the changes and process developments in the green steel to further optimize the refractory solutions.

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