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# Dissolution of refractories for gasification process of petroleum coke for the steel industry

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The production of energizing gases such as $H_2$ and CO by gasification process of solid fuels is a technology that has increased in recent years since it is an efficient and clean process. To enable the production of gases, it is necessary to use refractory materials capable of withstanding high temperatures, thermal shock and contact with aggressive media. Nowadays, there is not published literature on refractory materials used for furnaces lining for petroleum coke gasification at high temperatures (~1900 °C). Therefore, this paper deals with the study of alumina and magnesium aluminate/alumina-based refractories as candidates for the furnace lining used in the petroleum coke gasification for steel production. Refractory samples were made with some designed formulations which were subjected to chemical interactions with pellets made of petroleum coke and petroleum coke ash at 1650 °C for 4 h. After completing the tests, the formulations were cut transversely and were characterized by SEM-EDS and XRD to evaluate the resistance to slag penetration and formation of low melting point phases. The results show that slag penetration and corrosion in the refractory formulations occur due to the formation of hibonite, spinels ($Ni^{2+}$, $Fe^{2+}$, $Mg^{2+}$)(Al, Fe)$_2O_4$ and gehlenite phases. However, these phases together stop the molten slag penetration.



## 1. Introduction

Direct reduction of iron ore is a steelmaking process that is affected by the cost of natural gas, which highly increased in recent years in its operation cost, impacting significantly on the profitability of steel industries. Consequently, several companies have researched gasification processes of alternative fuels like biomass, coal and petroleum coke [1–5]. These processes have aroused great global interest in the scientific/technological community; therefore, many investigations have been conducted during the last decade which focused on using petroleum coke as a fuel source to produce electricity in a cleaner and more efficient way [6–9].

In a gasification process, usually known as synthesis gas or syngas for short, solid or liquid fuel chemically reacts with a gasification agent (air, oxygen or water vapor) at different temperature ranges depending on the type of the gasifier being used. The most useful way of classifying the gasifiers is by flow regime, i.e. the way in which the fuel and oxidant flow through the gasifier. They may be divided into three basic types groups: entrained flow, fluidised bed and moving bed. General characteristics of each type and the new Molten Iron Process (MIP) used in the steel industry are listed in Table 1.

Pulverized fuel or atomized oil flows co-currently with the oxidizing medium (typically $O_2$) in an entrained flow gasifier. The key characteristics of entrained flow gasifiers are their very high and uniform temperatures (usually more than 1000 °C) and the very short residence time of the fuel within the gasifier. For this reason, solids fed into the gasifier must be very finely divided and homogeneous, which in turn means that entrained flow gasifiers are not suitable for feedstocks such as biomass or wastes, which cannot be readily pulverized. Entrained flow gasifiers have been selected for nearly all the coal- and all the oil-based GPPs currently in operation or under construction.

Solids (e.g. coal and ash) in a fluidized bed are suspended in an upwardly flowing gas stream, which comprises the oxidant (normally air rather than $O_2$). The key feature of the fluidized bed gasifier (like the fluidized bed combustor) is that the fuel ash must not be allowed to become so hot that it melts and sticks together; if the fuel particles stick together, the bed will defluidize. The use of air as the oxidant keeps the temperature below ~1000 °C. Accounting for this fact, fluidized bed gasifiers are best suited to relatively reactive fuels, such as biomass.

The oxidant (steam and $O_2$) in a moving bed gasifier is blown into its bottom. The raw fuel-gas produced moves upward through a bed of solid feedstock, which gradually moves downwards as the

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**Table 1**
Comparison of gasifier types [10–12].

| | Conventional gasifiers | | | New development |
|---|---|---|---|---|
| | Entrained flow | Fluidized bed | Moving bed | MIP process |
| Fuel types | Solid and liquid | Solid | Solid | Solid |
| Fuel size (solid) | <500 μm | 0.5–5 mm | 5–50 mm | 0.5–5 mm[a] |
| Fuel residence time | 1–10 s | 5–50 s | 15–30 min | 1–10 s[a] |
| Gas outlet temperature | 900–1400 °C | 700–900 °C | 400–500 °C | 400–500 °C |
| Gas maximum temperature | ~1400 °C | ~1000 °C | ~1000 °C | ~1900 °C |

[a] Under investigation.

feed at the bottom of the bed is consumed. The defining characteristic of moving bed gasifiers is therefore counter-current flow. As the raw fuel-gas flows through the bed, it is cooled by the incoming feed, which in turn is dried and devolatilizes. Therefore, a very pronounced temperature profile can be observed in the gasifier from 1000 °C or more at the bottom to ~500 °C at the top.

In MIP process, explained in more detail later, the oxidant (steam and $O_2$) is blown together with pulverized petroleum coke into the bottom of the gasifier. The raw fuel-gas produced moves upward through a moving bed of solid feedstock composed of directly reduced iron (DRI) and fluxes. This bed gradually moves downwards as the feed at the bottom of the gasifier, where a fixed bed composed of metallurgical coke is smelted. As the raw fuel-gas flows through the DRI, it is cooled by the incoming feed and then it is heated and smelted. Hence, there is a very pronounced temperature profile in the MIP process, from ~1900 °C or more at the bottom to ~500 °C at the top. The defining characteristics of MIP process are the counter-current flow and a DRI smelter. In other words, it is a Smelter–Gasifier.

In any of the aforesaid types of gasifiers, the energy initially present in the fuel is transferred to the primary products of the process, so that the highest conversion to combustible gases, mainly $H_2$ and CO, as well as unwanted products such as tars, soot and ash [13–18] can be achieved. This gasification technology has gained great attention because of the feasibility to use a wide variability of combustible materials. It is also very environmentally friendly lower emission of pollutants compared with other sources used for energy.

Achieving high efficiency in a gasification process is not easy; to get this, it is indispensable to have an excellent lining in the gasifier furnace, in which the high temperatures chemical reactions of the process are conducted. This lining is usually composed of 2–6 layers of refractory materials, which vary in their chemical composition and density [19].

It is very important that the refractories show high operational performance, which is determined by their ability to withstand the chemical interactions in contact with aggressive media. On the other hand, good physical (density, melting temperature) and mechanical properties (resistance to thermal shock) are also required. Otherwise, if they do not meet these requirements, it might lead to damages due to corrosion/dissolution or slag penetration phenomena. The final result will be an intensive wear or spalling phenomena in the refractories that not only cause the failure of such gasifiers, but also cause the general process shutdown [20–23].

It is well known that the reliability of a refractory for specific applications is determined by its slag chemical attack resistance, erosion resistance, and their mechanical and thermal resistance during its operation. Although the slag may cause dissolution in the refractory (due to it penetrates from the refractory hot face through the porosity, favoring phases dissolution and promotes the formation of low melting point phases in solid solutions) and it affects in a negative way on its service life due to the weakening in the microstructure [24]; sometimes may also be useful in the process since if the slag does not react with the refractory material, it could form a protective coating against dissolution. On the other hand, besides typical affecting conditions in the refractory, it should be remembered that the temperature exposure plays an important role since it is a common factor in the refractory destruction.

Some studies have shown erosion phenomena in the refractory hot face when they have been employed with solid feedstock (coal or petroleum coke) in the lining of gasifiers. This is attributed to solid materials, since they tend to be abrasive when are injected at high speeds. Based on this fact, the service life of these refractories is estimated to be from 3 months to 2 years depending on injection conditions. It was also noted that the slag produced after the gasification of coal or petroleum coke generates an ash precipitation consisting mainly of oxides of Si, Fe, Al and Ca as well as elevated levels of K, Na, Mg, Ni and V [25].

Alumina and magnesia monolithic refractories in the presence of slag (60–75% $Na_2CO_3$, 20–38% $Na_2SO_4$, 1–4% $Na_2S$ and 1–4% $Na_2S_2O_3$) at a temperature of 900–1000 °C exhibited low chemical resistance. However, the mixture of both refractories (alumina–magnesia) showed good resistance by 20 h [26]. Finally, mullite, alumina and magnesium aluminate/alumina have been tested for chemical interactions in gasifiers in the presence of $H_2$, $H_2S$, CO and alkali at temperatures of 1000 °C for a period of 100 h. Results showed corrosion, erosion and thermal shock, as well as low melting point phases due to the presence of Na [27].

Nowadays, there is not literature reported on refractories used in furnaces lining for petroleum coke gasifiers for the steel industry, which can operate at the temperature of ~1900 °C. For this reason, it is highly relevant to develop high-performance refractories that could be implemented on the gasification process of petroleum coke since it involves aggressive conditions like high temperatures, reducing and oxidizing atmospheres and corrosive compounds generated during gasification as sulfur, iron oxide, vanadium pentoxide and nickel oxide which in contact with refractory materials generate low melting point phases.

The scheme presented in Fig. 1 shows the new process to be implemented in the steel industry, Molten Iron Process, MIP. This process involves three stages, which are as follows: the first one is the reduction of iron ore to produce sponge iron also called Direct Reduced Iron (DRI), which takes place in a direct reduction reactor; the second one is the gasification of petroleum coke with the DRI smelting and takes place in a gasifier furnace, and the third one is the refining of DRI to produce steel in the Electric Arc Furnace (EAF).

The gasification furnace is the process fulcrum point, since the reducing gases produced here are used in the Direct Reduction Reactor (DRR), and the hot metal obtained inside is the raw material for the EAF. The gasification of petroleum coke is carried out in this furnace to produce reducing gases such as $H_2$ and CO, see below Eq. (1), which will be fed into the direct reduction reactor for the production of DRI, see Eqs. (2) and (3) below which will be fed into the gasification furnace to produce high carbon hot metal.

$$\text{Petroleum coke} + H_2O(\text{steam}) + O_2 \rightarrow CO + H_2 + CO_2 + \text{ash} \quad (1)$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe^{\circ} + 3CO_2 \quad (2)$$

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe^{\circ} + 3H_2O \quad (3)$$

It is very important to mention that the current gasifiers operate at relatively low temperatures (see Table 1) in comparison with that intended to develop in the MIP process. Nevertheless, gasify