Analysis of changes in the chemical composition of the blast furnace coke at high temperatures

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Analysis and modelling

ABSTRACT

Purpose: The main purpose of this paper was to analyze the behavior of coke in the blast furnace. The analysis of changes in chemical composition of coke due to impact of inert gas and air at different temperatures was made. The impact of the application of the thermoabrasion coefficient on the porosity of coke was also analyzed.

Design/methodology/approach: By applying the Computer Thermochemical Database of the TERMO system (REAKTOR1 and REAKTOR3) three groups of substances can be distinguished. The chemical composition of blast furnace coke and the results of calculations of changes of chemical composition of coke heat treated under certain conditions were compared. The structural studies of these materials were presented.

Findings: The results of the analysis of ash produced from one of Polish cokes was taken for consideration. This is not the average composition of Polish coke ashes, nevertheless it is representative of most commonly occurring chemical compositions.

Practical implications: Thanks to the thermochemical calculations it is possible to predict ash composition after the treatment in a blast furnace. Those information was crucial and had an actual impact on determining the coke quality.

Originality/value: Presentation of the analytical methods which, according to author, can be very useful to evaluate and identify the heat treatment for blast furnaces cokes. The research pursued represents part of a larger project carried out within the framework of Department Extraction and Recycling of Metals, Czestochowa University of Technology.

Keywords: Blast furnace; Coke; Ash in coke; Thermochemical calsulations

1. Introduction

The years 1986-1998 witnessed the increase in the average usable volume Western Europe's blast furnaces from 1675 to 1780 m³. At the same time, the efficiency of pig iron production increased from 1.90 to 2.47 Mg/m³ per day during that period. Although the decrease in the unit consumption of fuels was small at that time, namely from 497 to 483 kg/Mg of pig iron, the drop in the consumption of coke was much greater, that is from 462 to 362 kg/Mg of pig iron (chiefly due to an increase in the amount of coal dust injected).

The increase in blast-furnace volume and the drop in the amount of coke per one ton of pig iron produced have spurred searches for the methods of improving the quality of coke. Indeed, with decreasing coke share in the charge the role of coke as a skeleton determining the gas permeability of the charge in the blast-furnace zones, where the iron-bearing part softens and melts, and also lower down the furnace, where it already drips as a primary slag, increases. Moreover, the coke performs also its role as a reducer and heat source.

The world's investigations into the suitability of coke for the blast furnace focus mainly on the determination of its strength properties, and thus resistance to grain degradation, conducted either by cold (e.g. MICUM or IRSID) or hot (e.g. CSR acc. to the Nippon Steel method) techniques. In the chemical composition of coke, the contents of undesirable ash constituents, such as alkalis, zinc, sulfur and phosphorus are primarily controlled. Recently, more and more consideration has been given to the humidity of coke and its contents of chlorine compounds [1].

2. The movement of materials in the blast furnace

In the upper part of the blast furnace, all charge components, i.e. ores (sinters, pellets), fluxes and coke are in a solid state. The flow of gases from the lower blast-furnace region upwards meets little diverse resistance. This resistance, or its converse - charge permeability, has been the subject of extensive studies for many years [2], and therefore the methods of controlling it are very well known. Technologies and techniques applied after World War II, such as the improvement of the ore sintering process, the development and application of the method of fine ores pelletizing and the improvement of coke production, have caused the graining of the blast-furnace charge and the stability of its grains loaded to the blast furnace to dramatically improve its gas permeability. Presently, to force gas through the lumped charge zone, or from the throat loading to the regions at temperatures of approx. 1100-1200°C, approximately 20% of the total pressure difference needed for forcing gas from the tuyeres to the throat is sufficient. So, if as much as 80% of the pressure of gas flowing through the blast furnace is lost for forcing the gas through the charge in the lower blast-furnace part, then it is essential to understand the mechanisms that determine resistances to flow in those lower zones.

The least gas permeability is exhibited by a zone, where charge lumps soften. This causes "sinking" of lumps and liquidation of voids between the lumps, and thus the disappearance of channels enabling the gas to flow within the charge, and, more specifically, within the ore. The zone of softening is called a "cohesion zone".

The charge is loaded into the blast furnace by layers of, alternately, ore and coke. This laminar structure still persists in the cohesion zone. As ore layers become less permeable, gases find their way of flow in the coke layers - that is why these locations of gas flow are called "coke windows" - see Fig. 1. The gas flows through these windows in a manner corresponding to the coke layer arrangement, that is almost horizontally [3].

A further increase in ore layer temperature makes the ore lying on the coke layer to flow down to the coke layer below it and flood the small channels between coke lumps - see Fig. 2. This causes a reduction in the coke window height.

The decreasing of the coke window must be counteracted by selecting ore (sinter) properties such, that the transition from their softening to melting state, i.e. flowing down the coke layer, proceed in the smallest possible temperature range. Investigations of different sinters [3] have shown that as the reduction of iron oxide progresses, the temperature range from softening to melting varies.

This explains the benefits obtained by using a basic sinter. Naturally, the progress of softening - melting depends on the properties of all charge components; so, it is not solely the sinter that should have a narrow softening - melting temperature range, but also the other ores and pellets should soften at similar temperatures.
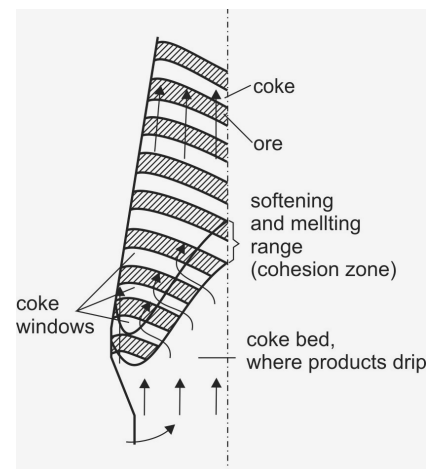

Fig. 1. Schematic diagram of the location of coke windows and the gas flow path in the blast furnace
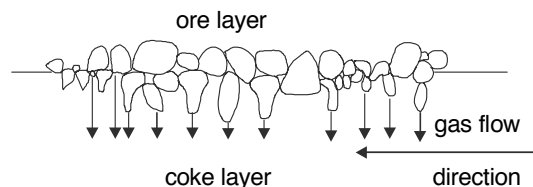

Fig. 2. Schematic diagram of primary slag penetration into the coke layer and the decrease in the height of a coke window facilitating the flow of gas

Sinters of a small CaO/SiO_2 basicity, i.e. of up to 1.0, clearly extend this range; whereas sinters with a basicity greater by a factor of 1.5 or more retain the original size of this range as reduction progresses.

3. Thermodynamic calculations

The purpose of thermodynamic calculations was to determine chemical composition of the products of the reaction of interaction of coke ash mineral constituents with elementary carbon and air and also the behavior of coke at high temperatures in the conditions of neutral gas (argon). The following calculation conditions were assumed:

- the reaction system is a closed system,
- reactions attain the condition of chemical equilibrium,
- the pressure is constant (p = 1.5 atm), while the temperatures vary in the range from 1300 K to 2500 K,
- chemical composition of 9.8% of ash in the coke: Fe - 8.8 %; Mn - 0.12 %; P - 0.590 %; S - 0.67 %; SiO_2 - 40.0 %; Al_2O_3 - 26.5 %; CaO - 7.2 %; MgO - 3.6 %, H - 0.3%; N - 0.6%; K_2O - 1.8%; Na_2O - 1.8%.
- it was preliminarily assumed that several dozens different chemical compounds, either gaseous or condensed, might occur among the reaction products,
- thermochemical data for particular substances were taken from the Computer Thermochemical Database of the TERMO system.

Two computer programs, REAKTOR1 and REAKTOR3, were used for calculations, both of them relying on the Gibbs free energy minimization method. The former of the programs utilizes an algorithm based on the Lagrange function, while the latter uses the penalty function method. The latter program was employed in situations, where numerical difficulties associated with the lack of the method's convergence occurred (which, in principle, prevented the problem set to be solved by the classical Lagrange method). In the gaseous phase, three groups of substances can be distinguished:

1) compounds (elements), whose fraction increased with the increase in temperature;
2) compounds (elements), whose fraction decreased with the increase in temperature;
3) compounds (elements), whose fraction remained at a constant level with the increase in temperature.

The results are presented in the form tables. These detail chemical compounds that can form between coke ash constituents under the action of high temperatures and a chemical medium with a different fraction of reducing atmosphere (the calculation conditions: coke + argon atmosphere, coke + air).

It can be seen from the summary (Tables 1, 2) that Mg_2SiO_4 and FeSi occur in the whole temperature range, regardless the calculation variant (Fig. 3, Fig. 4).

Table 1.
Variations of substances occurring in the coke-air system in a temperature range of 1400-1800 K

Substance	1400 K	1500 K	1700 K	1800 K	Melting point [K]
$CaO·Al_2O_3·2SiO_2$	present	present	present	present	1823
$2CaO·Al_2O_3·SiO_2$	absent	absent	absent	absent	1857
$SiO_2·Al_2O_3$	present	present	present ↓	present ↓	1800
$CaO·2Al_2O_3$	absent	absent	absent	absent	2053
$2MgO·SiO_2$	present	present	present	present	2171
$2FeO·SiO_2$	absent	absent	absent	absent	1493
SiC	absent	absent	absent	absent	3103
CaS	absent	absent	absent	absent	2798
$K_2O·4SiO_2$	present	present	absent	absent	1043
Al_2O_3	absent	absent	absent	absent	2327
FeSi	present	present ↑	present ↑	present ↑	1683
$Na_2Si_2O_5$	present	present	absent	absent	1147

Note: ↑ - increasing substance concentration, ↓ - decreasing substance concentration

Table 2.
Variations of substances occurring in the coke-argon system in a temperature range of 1400-1800 K

Substance	1400 K	1500 K	1700 K	1800 K	Melting point [K]
$CaO·Al_2O_3·2SiO_2$	present	present	absent	absent	1823
$2CaO·Al_2O_3·SiO_2$	absent	absent	present	absent	1857
$SiO_2·Al_2O_3$	present	present	absent	absent	1800
$CaO·2Al_2O_3$	absent	absent	present	present	2053
$2MgO·SiO_2$	present	present	present↓	absent	2171
$2FeO·SiO_2$	absent	absent	absent	absent	1493
SiC	absent	absent	present	present	3103
CaS	absent	absent	present	present ↑	2798
$K_2Si_4O_9$	present	present	absent	absent	1043
Al_2O_3	present	present	present	present ↑	2327
FeSi	present	present	present	present	1683
$Na_2Si_2O_5$	absent	absent	absent	absent	1147

Note: ↑ - increasing substance concentration, ↓ - decreasing substance concentration

To a lesser extent, other substances occur, such as: $CaO \cdot Al_2O_3 \cdot 2SiO_2$, $SiO_2 \cdot 2Al_2O_3$ and $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $CaO \cdot Al_2O_3$. A similar situation is true for Al_2O_3, SiC, and CaS. Sodium and potassium, in the range of temperatures not exceeding 1600 K, can form the following silicates: $Na_2O \cdot 2SiO_2$ and $K_2O \cdot 4SiO_2$, which undergo decomposition at higher temperatures.

Therefore, in the conditions under consideration, sodium and potassium occur in their respective vapors. The gaseous phase of the analyzed systems includes the following main components: CO and N_2 or CO and Ar. The concentration of CO_2 was much lower, ranging from 0.00002 vol.% to 0.04 vol.%. The remaining components of the gaseous phase were in even lower concentrations; these included: SiO, PS and the vapors of metals, such as: Na, K, Mg, Fe, and Mn.

The variations in the carbon monoxide content of argon lay in the range from 0.3 to 2.4 g/kg of the working substance, while in air, in the range from 128 to 130 g/kg of the working substance. Similarly, the CO_2 contents for the inert gas ranged from $2.1 \cdot 10^{-5}$ to 0.0004 g/kg of the working substance, while for air, from 0.02 to 0.6 g/kg of the working substance.
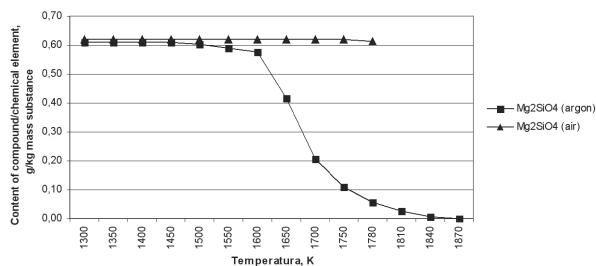

Fig. 3. Variations in Mg_2SiO_4 concentration in coke ash in a temperature range of 1300-1870 K
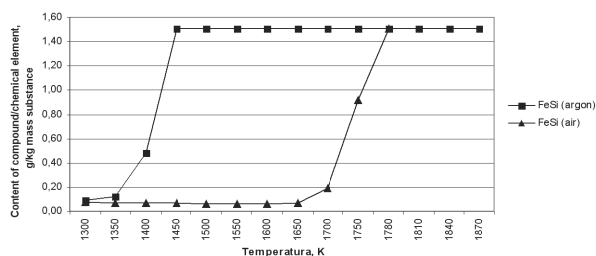

Fig. 4. Variation in FeSi concentration in coke ash in a temperature range of 1300-1870 K

From the calculations for cases, where the behaviour of coke under inert conditions - argon and in air with oxygen was examined, it was found the forming gaseous components had different concentrations (Figs. 5-7).

The situation for the occurrence of condensed phases in the coke material subjected to thermal action with the participation of argon (Fig. 8) and air with oxygen (Fig. 9) presented itself differently. A higher variability of the compounds was found for the contact of coke with air than for its contact with argon. The following compounds were found to have occurred: Al_2SiO_5,

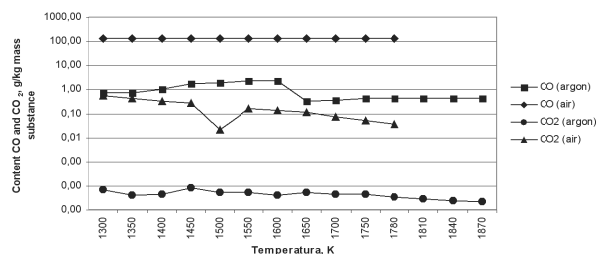$MgSiO_3$, Na_2CO_3 and K_2CO_3. This was due to the oxygen content of the air with oxygen.

Fig. 5. Comparison of changes in CO and CO_2 for the thermal effects of coke with argon and air in the temperature range 1300-1870 K
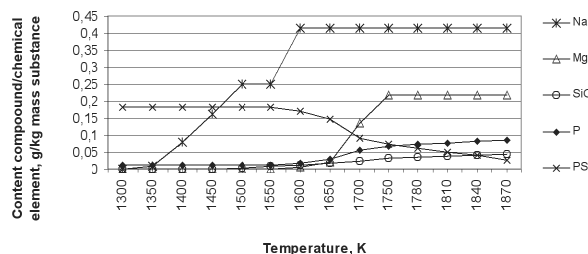

Fig. 6. Changes in the content of gaseous components in the temperature range 1375-1700 K in inert gas – argon
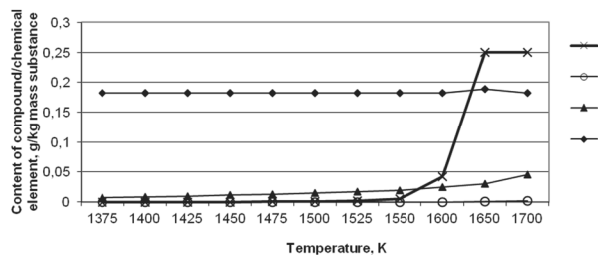

Fig. 7. Changes in the content of gaseous components in the temperature range 1300-1870 K in air with oxygen

The analysis of porosity of surface for the samples presented in Table 3. This porosity of coke depends primarily on the grade of coal used for coke production (ie. the content of volatile matter and the resilience of puffing) and method of preparing coal for the coking process (mainly from coal fineness and density of the solid carbon).

The analysis the uniformity of distribution of macropores and the weakened area inside the grain coke after heating were a more meaningful assessment of the suitability of coke for blast furnace process. The tests of assessment of the grain structure of coke were also performed. These tests were made with confocal microscope OLYMPUS 3300.
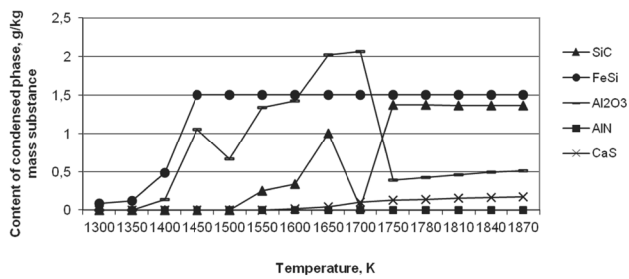
Fig. 8. Changes in content of component condensed matter contained in the coke after the thermal effects of argon in the temperature range 1300-1870 K
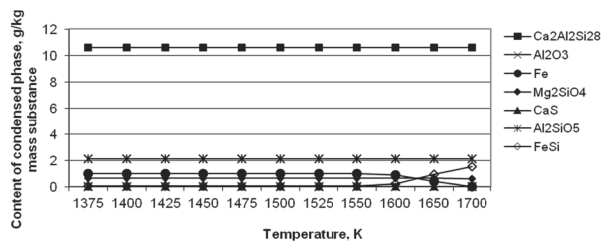

Fig. 9. Changes in content of component condensed matter contained in the coke after the thermal effects of air with oxygen in the temperature range 1375-1700 K

Table 3.
Porosity of surface for the samples from Coke Plant

Nr of test	Characteristic of specimen	Thermoabrasion coefficient [g/min]	Porosity of surface [%]
1	before heating	9.31	68.2
1	after heating	9.31	76
2	before heating	10.52	75.1
2	after heating	10.52	69.9

The sample of the grain structure is shown in Fig. 10. These observations were confirmed in a study for cokes in the pre-tuyère chamber model method (known also as the thermoabrasion method).

4. Conclusions

The thermodynamic calculations enabled the determination of chemical composition of the products of the interaction reaction of ash mineral constituents with elementary carbon. The results of the analysis of ash produced from one of Polish cokes was taken for consideration. This is not the average composition of Polish coke ashes, nevertheless it is representative of most commonly occurring chemical compositions.

The number of compounds forming from the constituents of coke ash when heated in a stream of gases with a highly diverse reducing capacity reflects the complexity of the physicochemical phenomena. These phenomena might be, to a large extent, responsible for the destruction and weakening of the proper structure of coke.

The precise explanation of how the behavior of thermal grindability varies depending on the complex structure of mineral compounds transformed at a high temperature and under an active interaction of the gaseous phase of variable reducing capacity required further investigations.
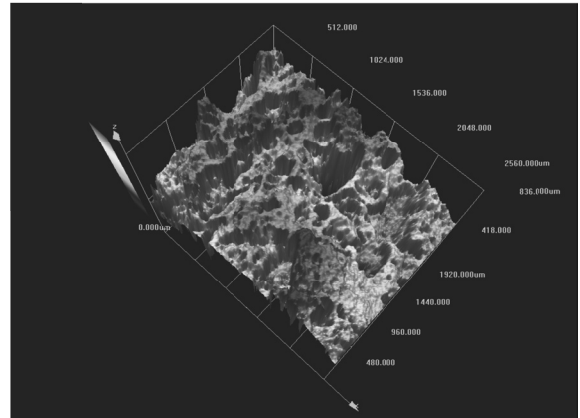
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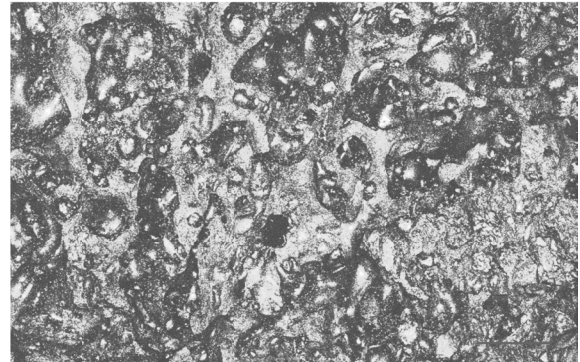
b)

Fig. 10. The structure for coke from bearings: a) the structure, b) the determinant of size for pores

Acknowledgements

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