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THE EFFECT OF TEMPERATURE AND CO₂ CONCENTRATION IN REACTION GAS ON COKE REACTIVITY

WPŁYW TEMPERATURY I ZAWARTOŚCI CO₂ W GAZIE REAKCYJNYM NA REAKCYJNOŚĆ KOKSU

The relationships between coke reactivity and CO₂ concentration in reaction gas as well as between coke reactivity and temperature of examination were investigated. The results of coke reactivity examinations at the temperatures range from 900°C to 1050°C with the CO₂-content in reaction gas being equal to 19,6%, 44,4%, 76,8% and 100% are presented. Two cokes with different reactivity, determined under standard conditions, were tested. It was shown that coke reactivity depends significantly on both, CO₂- content in gas and the temperature of examination. These correlations constitute an individual feature of coke. Coke reactivity decrease remarkable with decreasing of CO₂ concentration in gas. It was stated the linear correlation between coke reactivity and CO₂ concentration. The correlation between reactivity of the examined cokes and the temperature of examination is of exponential type.

The obtained results indicate that coke reactivity in the direct reduction zone of the blast furnace could be different from that determined as the value characterizing coke properties under standard conditions. This is a result of lower CO₂-content in gas in the blast furnace and the wide range of temperatures at which the direct reduction process occurs. Therefore, it is possible that the reactivity of coke may not be the main criterion of evaluating its suitability for the blast furnace process.

Badano zależność reakcyjności koksu od stężenia CO₂ w gazie reakcyjnym i temperatury. Przedstawiono wyniki badań reakcyjności koksu w zakresie temperatur od 900°C do 1050°C oraz zawartościach dwutlenku węgla w gazie reakcyjnym wynoszących: 19,6%, 44,4%, 76,8% i 100%. Przedmiotem badań były dwa koksy o różnej reakcyjności oznaczonej w warunkach standardowych. Wykazano, że reakcyjność koksu istotnie zależy zarówno od zawartości dwutlenku węgla w gazie i od temperatury oznaczenia. Zależności te są indywidualną cechą koksu. Reaktywność koksu znacząco maleje wraz ze zmniejszeniem

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stężenia CO_2 w gazie reakcyjnym. Stwierdzono liniową zależność reakcyjności koksu od stężenia CO_2 w gazie. Zależność reakcyjności badanych kokсів od temperatury oznaczenia ma charakter wykładniczy.

Otrzymane rezultaty wskazują, że reakcyjność koksu w strefie redukcji bezpośredniej wielkiego pieca może być inna od wyznaczanej jako wielkość charakteryzująca własności koksu w warunkach standardowych. Wynika to z mniejszej zawartości dwutlenku węgla w gazie w wielkim piecu i szerokiego zakresu temperatur w której zachodzi redukcja bezpośrednia. Zatem reakcyjność koksu wielkopiecowego może nie być podstawowym kryterium oceny jego wartości użytkowej.

1. Introduction

Coke is the only blast furnace material which in its solid state moves from the top of the furnace to the tuyere zone. This enables the flow of gas originating in the tuyere zone in counter-current stream to the moving iron-bearing charge. The role of coke as the material determining the permeability of charge is especially important in the part of the blast furnace where the remaining materials turn into the plastic state. Minimization of the unit consumption of coke thanks to substitute fuels (usually pulverized coals, injected through the tuyeres of the blast furnace) makes coke quality crucial. Above all, this concerns the size distribution of skip coke and its resistance to changes in this respect caused by a number of factors affecting coke during its movement down to the tuyere zone. The following factors are of crucial importance:

- mechanical impact of the iron-bearing charge on coke. Abrasion of coke lumps and blowing-out of the resulting fines with the blast furnace gas are a consequence of this impact,
- compression by charged materials. It is weak, though (about 10 kg/cm^2), and does not exert a significant influence upon degradation of coke lumps whose resistance to compression is at least 15 times greater,
- influence of temperature, especially higher one than that at which the coking process ends (about 1000°C). The consequences of the influence of temperature on coke moving from the top of the blast furnace down to the tuyere zone were presented in work [1],
- interaction of liquid pig iron and slag with coke,
- effect of gas with changing chemical composition on coke occurring at a changing temperature.

All these factors have a characteristic effect on the changes in physical and chemical properties of coke moving from the top of the blast furnace down to the tuyere zone and can cause a change in its size distribution.

This work focused on investigating the effect of temperature and CO_2 — content in gas on coke reactivity. Coke reactivity is most often determined by using CO_2 as an oxidizer. This is justified if we consider the oxidizing influence of CO_2 , formed as a result of the indirect reduction of iron oxides, on coke in the blast furnace. The course of the reaction of carbon contained in coke with carbon dioxide occurring in gas in the

blast furnace can be expressed as: $\text{CO}_2 + \text{C} = 2\text{CO}$. It is a reversible, heterogeneous, and superficial reaction. The rate of such a reaction depends on:

- temperature at which it occurs,
 - CO_2 -content in gas interacting with coke,
 - gas pressure,
 - area of coke surface, which takes part in the reaction, i.e. active surface of coke.
- The effect of these factors on coke reactivity has been thoroughly investigated [2, 3, 4, 5].

At present, two standard methods are used to determine coke reactivity: the Geneva method and the Nippon Steel Corporation method (NSC) [6, 7]. In both cases, CO_2 is the oxidizer. In the Geneva method, coke reactivity is determined at the temperature of 1000°C using a coke sample containing grains of $1\div 3,15$ mm. The mass of the coke sample is 7g. The time of determination is equal to 15 minutes. The volume of the CO_2 consumed during the reaction in cm^3 per 1g of coke in one second is the measure of coke reactivity. The loss of coke sample mass is not examined. It can be calculated by using the volume of the CO_2 consumed during the reaction. The NSC method involves the determination of coke reactivity at 1100°C using a coke sample with the mass of 200g containing 20 mm grains (± 1 mm). Grains of 20 mm still have the porosity of the initial coke [5]. The time of examination is equal to 2 hours. The loss of coke mass (in %) is the measure of coke reactivity. Additionally, this method entails the determination of coke strength after determining the reactivity. As a result of the oxidizing reaction of carbon dioxide with coke, there occurs a partial burning of carbon, which results in a decrease in strength.

From the brief outline given above, it can be concluded that these methods, though markedly different, can still be successfully used for comparative evaluation of the reactivity of cokes. However, only to a limited extent do the results of determining coke reactivity by means of these method, enable drawing conclusions about the true consumption of coke in the blast furnace due to the Boudouard reaction. This is chiefly a consequence of the fact that the real CO_2 -content in gas reacting with coke in the blast furnace is smaller than that applied in both methods. Moreover, this interaction takes place within a wide temperature range. It is impossible to evaluate the CO_2 -content in gas interacting with coke explicitly. With great simplification, it is possible to establish by calculation that the maximal CO_2 content in gas in the blast furnace can reach $42 \div 45\%$ [8]. If the entire amount of the resulting carbon monoxide (CO) were consumed by leaps as a result of indirect reduction of iron oxides, the maximal content of the resulting CO_2 in gas interacting with coke would be equal to about 45%. In the real conditions of the blast furnace, such a situation is impossible because the CO_2 formed as a result of the indirect reduction ($\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$) reacts with coke carbon bringing carbon monoxide back ($\text{CO}_2 = \text{C} + 2\text{CO}$). Then, the CO_2 — content in gas reacting with coke will always be smaller than 45%. The temperature, at which CO_2 reacts with coke, also will not be equal only to 1000°C or 1100°C at which coke reactivity is determined. Hence, coke reactivity under true conditions of the blast furnace may be different from that determined according to the applied standards.

2. The aim and scope of investigations

This work aims at investigating the dependence of the extent of coke carbon gasification both on the CO₂ — content in gas and on the temperature at which this agent reacts with coke. Two cokes were examined (marked as: coke 1 and coke 2) which differed in their physical and chemical properties, particularly reactivity determined by the standard Geneva and NSC methods. The characteristics of the cokes is given in Table 1.

Coke characteristics

TABLE 1

Coke number	Moisture %	Ash content %	Volatile matter content %	Reactivity (Geneva method) cm ³ /g.s	Reactivity and strength (NSC method)		
					CRI %	CSR %	CSR before determination of CRI %
1	2	3	4	5	6	7	8
coke 1	0.4	10.3	0.5	0.30	27.9	60.2	84.7
coke 2	0.6	11.1	1.5	0.54	47.2	40.8	86.1

In order to gain knowledge about the relationship between coke reactivity and the CO₂ -content in gas reacting with coke, reactivity was determined with the CO₂ -content in gas being equal to: 19,6%, 44,4%, 76,8% and 100%. A mixture of nitrogen and carbon dioxide was applied. The determination was carried out using the equipment and following the procedures specified by the Geneva and NSC methods [6, 7]. The influence of temperature on the reactivity of the cokes was established by determining reactivity by the Geneva method at the temperatures of: 900°C, 950°C, 1000°C and 1050°C. Gas with a content of CO₂ equal to 100% was used. The calculation of the coke reactivity index in the case of experiments carried out by the Geneva method was based on the following relationship [6]:

$$-K = \frac{VT}{mT_0} \left(2 \ln \frac{2 - \frac{C}{C_0}}{1 + \frac{C}{C_0}} + \frac{1 - \frac{C}{C_0}}{1 + \frac{C}{C_0}} \right), \quad (1)$$

where:

K — reactivity index, cm³/ g.s

M — mass of sample, g

V — gas flow rate, cm³/ s

T — temperature of reaction, K,

T₀ — temperature of the CO₂ entering the retort, K

C — CO₂ concentration in the gaseous product of reaction, %

C₀ — CO₂ concentration in the entering gas, %.

3. Results and discussion

Coke reactivity determination by the Geneva method according to standard [6] has to be carried out with the CO_2 -content in the reaction gas equal to 100%. Reactivity index K determined with the use of gas of a different CO_2 concentration give information only about the extent of coke carbon gasification at a pre-set CO_2 — content. The value of the reactivity index K is given as an average value from the measurement period of 15 min.

Figure 1 represents the relationship between the reactivity index K and time of determination. From this relationship it can be concluded that, as the time of determination goes on, coke reactivity decreases. The drop in the reactivity index between minute 1 and minute 16 is equal to $0,05 \div 0,07 \text{ cm}^3/\text{g} \cdot \text{s}$. This is a result of intensive oxidation (burning out) of more active centers of the coke surface in the initial period. The dwindling of these centers stabilizes coke reactivity. In the examined cokes, this stabilization occurs in minute 11 for coke 1 and in minute 14 for coke 2. Hence, the assumption of the mean value of K while calculating the reactivity index is fully justified.

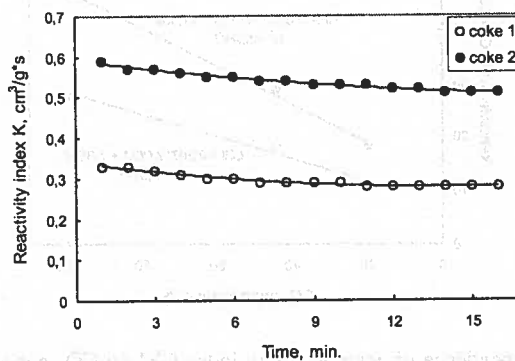


Fig. 1. Dependence of coke reactivity index K on time of estimation

Figure 2 and Figure 3 represent the correlation between the reactivity index of the examined cokes and CO_2 concentration in the reaction gas, determined by the Geneva and NSC methods, respectively. It can be noted that the reactivity of coke drops with the decrease in the CO_2 content in gas. The mean reactivity index K for coke 1, determined with the CO_2 — contents in gas equal to 100%, 44,4% and 19,6%, are 0,30, 0,15 and 0,10 $\text{cm}^3/\text{g} \cdot \text{s}$, respectively. The reactivity indices for coke 2, determined under similar conditions, are equal to 0,54, 0,31 and 0,20 $\text{cm}^3/\text{g} \cdot \text{s}$, respectively. The difference between coke reactivity index determined with the CO_2 - content in gas equal to 100% and 19,6% equals 0,20 $\text{cm}^3/\text{g} \cdot \text{s}$ for coke 1 and 0,34 $\text{cm}^3/\text{g} \cdot \text{s}$ for coke 2. Hence, it may be concluded that, under conditions of the occurrence of the $\text{CO}_2 + \text{C} = 2\text{CO}$ reaction in the blast furnace, coke reactivity can be even two times smaller than that determined under conditions specified by standards.

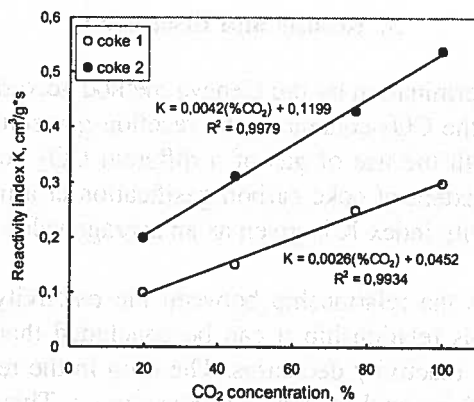


Fig. 2. Dependence of coke reactivity index K on CO₂ concentration

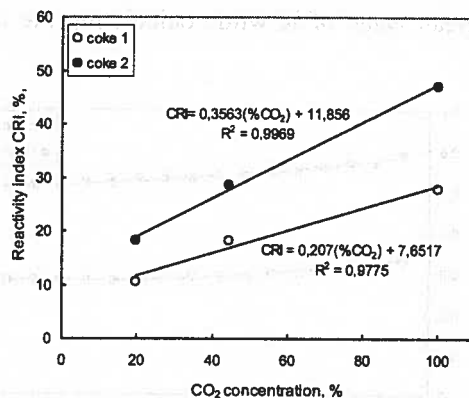


Fig. 3. Dependence of coke reactivity index CRI on CO₂ concentration

The relationships between coke reactivity and the CO₂ -content in the reaction gas are linear for the examined range of CO₂ concentration. The course of this relationship is, however, different for each of the examined kinds of coke. Hence, it can be inferred that this dependence constitutes a distinctive feature of each coke. In the case of the coke with a higher reactivity (coke 2), the CO₂-content in gas has a greater effect on the rate of the Boudouard reaction, which will result in a higher coke consumption during the direct reduction process.

Figure 4 represents the obtained correlations between the coke strength index (CSR) of the examined cokes, found after determining the CRI, and CO₂ concentration in the reaction gas. It can be seen that a growth in the CO₂ concentration results in a decrease in the determined coke strength index. The observed difference in strength between coke 1 and coke 2 increases with the growth of the CO₂ concentration. Similarly to the above-mentioned relationship between the reactivity and the CO₂ concentration

in gas, the dependence of the CSR on the CO₂ concentration is a distinguishing feature of coke.

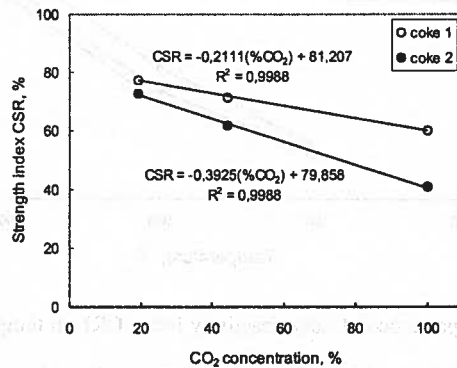


Fig. 4. Dependence of coke strength index CSR on CO₂ concentration

The temperature of examination is an important factor determining coke reactivity. The correlation between this temperature and the reactivity index K is represented in Figure 5 and Figure 6 for coke 1 and coke 2, respectively. It can be observed that the reactivity depends significantly on the temperature of examination. In the temperature of 900°C the reactivity of both cokes is negligible. At this temperature, the reactivity index is equal to 0,05 cm³/g·s for coke 1 and 0,10 cm³/g·s for coke 2. With the growth of temperature, the reactivity of both cokes increases and, at the temperature of 1000°C, it is equal to 0,30 cm³/g·s for coke 1, and to 0,54 cm³/g·s for coke 2. This means that, approximately, the reactivity grew fivefold.

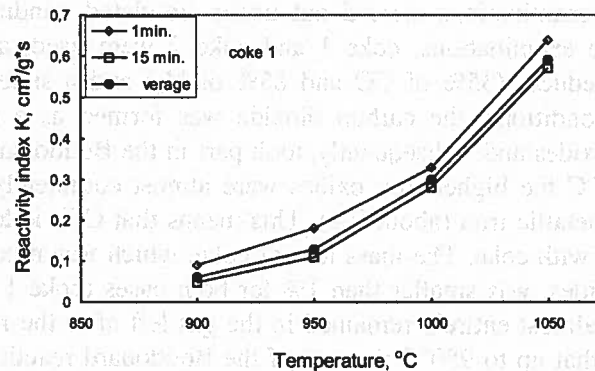


Fig. 5. Dependence of coke reactivity index K on temperature

The correlation between the coke reactivity and the temperature of examination, as it can be inferred from Figure 5 and Figure 6, is not of linear type. This can be attributed to both, the lack of the equilibrium state of the reaction $CO_2 + C = 2CO$

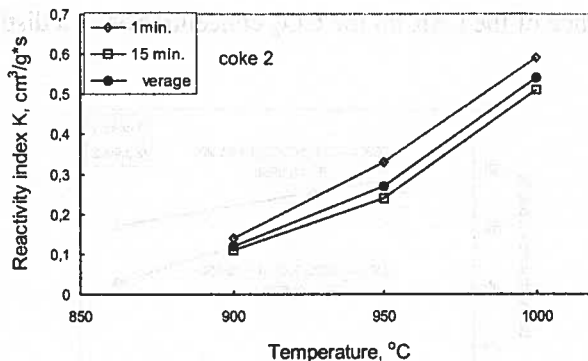
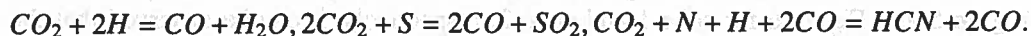


Fig. 6. Dependence of coke reactivity index CRI on temperature

resulting from the conditions of the determination, and to the changes in physical and chemical properties of coke due to the temperature at which reactivity is examined. It should be remembered that, apart from carbon, the coke organic matter contains hydrogen, nitrogen, sulphur and oxygen. So, carbon dioxide can react also with these elements, which, in a simplified way can be expressed as follows:



Moreover, as a result of heating of coke at a temperature higher than the final coking temperature, the carbon contained in it undergoes the graphitization phenomenon [3]. This fact may have an effect on the value of the determined reactivity index K and, in consequence, on the non-linear character of the function K versus T.

The possibility of carbon dioxide reacting with coke carbon, as well as the above mentioned influence of the temperature on the course of the reaction was proved also during laboratory examinations carried out under simulated conditions of the blast furnace [9]. In the examinations, coke 1 and coke 2 were used, as well as carbon monoxide as the reducer (35% of CO and 65% of N₂) and a sinter containing iron oxides. In these conditions, the carbon dioxide was formed as a result of indirect reduction of iron oxides and, subsequently, took part in the Boudouard reaction. It was shown that at 950°C the higher iron oxides were almost completely reduced to FeO and partly to the metallic iron (about 8%). This means that CO₂ is formed, which can subsequently react with coke. The mass loss of coke, which was mixed with the sinter containing iron oxides, was smaller than 1% for both cases (coke 1 and coke 2), and the resulting CO₂ almost entirely remained in the gas left after the reaction. Hence, it can be concluded that up to 950°C the rate of the Boudouard reaction was negligible. The experiment at 1100°C showed a similar extent of sinter reduction. However, a significant loss in coke mass occurred (coke 1 ca. 7%, coke 2 ca. 11%). The result of the experiment, then, is in accordance with the above-mentioned examinations which indicate that coke reactivity at 1100°C is much higher than at 950°C.

The rate of the Boudouard reaction in the blast furnace depends not only on temperature but also on the possibility of contact of coke with the flowing gas. In the

zone of softening- melting of the sinter, the rate of CO_2 reaction with coke slows down. It is assumed that the distribution of the reaction rate resembles normal distribution, with the maximum at the temperature of the upper limit of the cohesion zone, i.e. within the range of $1225 \div 1250^\circ\text{C}$, depending on the materials being used [10]. For this range of temperatures, coke reactivity can be far greater than that determined according to applied standards. In particular, this concerns cokes with high reactivity.

Gas pressure in the blast furnace is an additional factor influencing coke reactivity in industrial conditions. This factor, however has no significant effect on the course of the coal gasification reaction. An increase in pressure results in a growth of equilibrium partial pressure of CO_2 reacting with coke, which means a drop in the reaction rate and in the amount of CO_2 that has undergone the reaction. However, this change is small. For instance, a change in pressure from 1 atmosphere to 3 atmospheres at 1000°C causes a change in the CO_2 equilibrium concentration by about 0,06% with the initial CO_2 concentration equal to 19,6% and 1,4% with the initial concentration of CO_2 equal to 100%. With the growth of temperature the effect of pressure becomes less powerful. At 1200°C the change in the equilibrium concentration of CO_2 is about 0,01% with the initial concentration of CO_2 equal to 19,6% and about 0,15% with the initial concentration of CO_2 equal to 100%.

The coke reactivity and coke strength indices determined by the NSC standard (CRI and CSR) are a commonly used criterion for evaluating coke quality. Determination of these indexes enables a quality comparison of the produced coke. However, the usefulness of the indexes determined according to the standard may be limited in the real blast furnace process. In particular, this concerns coke reactivity.

It can be inferred from the relationship between the coke reactivity index and CO_2 concentration, shown in Figure 2 and Figure 3, that the difference between reactivity determined for both the examined cokes diminishes with the decrease of the CO_2 concentration in gas. Hence, the recorded significant difference in reactivity of the cokes, determined according to the standard (100% of CO_2) can become small when the CO_2 concentration is low. This difference can change depending on temperature, but it is still smaller than that in reactivity determined according to the standard.

Under true conditions of the blast furnace operation, for temperatures exceeding 1000°C , the CO_2 concentration in gas is close to the smallest value used for the purposes of the examinations. Major carbon consumption during coke movement in the blast furnace will occur at temperatures exceeding 1000°C as a result of direct reduction $\text{FeO} + \text{CO} = \text{Fe} + \text{CO}_2$ and $\text{CO}_2 + \text{C} = 2\text{CO}$. Model calculations for real periods of the blast furnace operation showed that within the above-mentioned temperature range, about 50% of FeO is reduced in the process of direct reduction [11]. So, about 50% of the CO_2 formed as a result of the reduction process reacts with coke carbon. Relating this value to the amount of carbon dioxide which can theoretically be present in blast furnace gas (45%), the real concentration of CO_2 in the zone of the Boudouard reaction equals to about 20%. It can, therefore, be expected that coke reactivity, with such a CO_2 concentration, will be different from that determined during coke examination. Hence, coke gasification will be smaller accordingly. In the indirect reduction zone

of the blast furnace, at the temperatures below 1000°C, coke carbon gasification is negligible or does not occur at all. It seems, then, that attaching too much importance to the reactivity of blast furnace coke is unfounded. In the real conditions of the blast furnace, coke carbon consumption as a result of the Boudouard reaction should be lower than that expected from standard examination of coke reactivity.

Coke reactivity evaluation is a hint providing information about the possibility of coal gasification and the amount of coke consumed in the process of direct reduction. The conditions of laboratory determination of coke reactivity are much different from thermal and chemical conditions in the blast furnace. This concerns the effect of two contrary factors: CO₂ concentration which is different from that defined by standards, and temperature. Despite the compensating action of these factors, coke reactivity determined under laboratory conditions may be different from that in the blast furnace. Therefore, the usefulness of the determined indices may be restricted to a comparison of coke quality and qualitative evaluation of coke reactivity in the blast furnace. Fulfillment of the most important role of coke in the blast furnace, i.e. ensuring proper permeability of charge, will depend mainly on the size distribution and mechanical properties of skip coke. In the blast furnace operation, coke with high strength and appropriate reactivity is preferred. Coke reactivity can influence its unit consumption. High coke reactivity will result in an increased share of the direct reduction process, and, in consequence, higher unit consumption of coke. This is a fundamental reason why coke with low reactivity is preferred, and not the fear of coke strength decreasing as a result of excessive consumption of carbon, with coke reactivity being high.

4. Conclusions

1. Coke reactivity depends significantly on both the CO₂ content in the reaction gas and the temperature of examination. These relationships constitute a distinctive feature of coke.
2. Coke reactivity decrease with decreasing of CO₂ concentration in gas. The correlation between coke reactivity and CO₂ concentration is of linear type.
3. Reactivity of the examined cokes increase exponentially with rising the temperature of determination.
4. Coke reactivity in the direct reduction zone of the blast furnace may be different from that determined according to the standard characterizing coke quality. This results from the CO₂ -content in gas in the blast furnace being lower than that defined by the standard and the wide temperature range of the direct reduction process. Hence, it is possible that the reactivity of coke determined according to the applied standards will not be a criterion for evaluating its suitability for the blast furnace process.

Acknowledgements

This work was supported by Ministry of Science and Information at AGH University of Science and Technology under DS fund No. 11.11.210.62.

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Received: 10 February 2005.