

THE EFFECT OF K_2CO_3 ON THERMAL OXIDATION OF COKES AND CARBONACEOUS MATERIALS

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The effect of K_2CO_3 on thermal oxidation of the blast furnace cokes and carbonaceous materials in the air was investigated by means of thermal analysis. The results obtained from the thermal analysis showed that coke contains two carbonaceous structures. The addition of K_2CO_3 affected mainly oxidation of a less ordered structure while the second stage oxidation went without changes. With increasing concentration of an additive, a decrease of both the characteristic temperatures and the values of activation energy occurred together with enhancement of reaction heat. The catalytic effect of potash on the oxidation of materials with variously ordered carbonaceous structure grows with no order of carbonaceous matter. In all cases (except graphite) the addition of potash caused a decrease of activation energies.

Keywords: coke, K_2CO_3 , thermal oxidation, kinetics, carbonaceous materials, thermal analysis

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1. Introduction

Coke degradation in the blast furnace is a very complicated process. Even partial knowledge about its course has considerable technological and economic significance. The mechanical, chemical and thermal action on the blast furnace coke causes a decrease in its strength. Namely these are the surface reactions of carbon matter of coke with gaseous phase [1].

It was also found that the behavior of coke is considerably influenced by the reactions between the carbon matter and its ash under the highest temperatures [2-6]. At these temperatures the coke is graphitized, which is another mechanism of coke degradation.

The degree of coke degradation is mainly affected by the presence of alkalis [7] where the catalytic effect of alkali carbonates to the Boudouard reaction was unambiguously proved [8-9]. The enhanced alkali content distinctively increases coke reactivity under high temperatures and decreases its strength [10].

In the last ten years the action of alkalis on the blast furnace processes has been intensively investigated [11]. There are new findings about accumulation of alkali compounds in the lower part of blast furnace and their subsequent circulation.

Potash is one of the most effective catalysts in the coal gasification process [12]. In order to understand the mechanism of its action it is necessary to know the behavior of a separate compound depending on the atmosphere or temperature [13]. A lot of studies interested in these problems, however, observe properties of K_2CO_3 in the blend with other inorganic materials [14].

The results obtained in [15] which deals with coke thermal oxidation in the presence of ZnO, PbO, Fe_2O_3 , $CaCO_3$ and K_2CO_3 proved that PbO and K_2CO_3 have the most distinct effect on coke oxidation in the air. But these two substances differ in the catalytic action mechanisms.

The aim of this paper was to look into the effect of K_2CO_3 , which is effective catalyst in the gasification process, on the oxidation of cokes and carbonaceous materials using a method of thermal analysis. Unfortunately, only few papers deal with behavior of potash separately, most studies follow up properties of K_2CO_3 in the blend with other inorganic compounds. To explain the catalytic effect of potash, three factors were selected: different concentration of K_2CO_3 , varied carbonaceous structure and cokes with variant reactivity. The activation energies of oxidation reactions of measured materials were determined by the method of direct non-linear regression [16].

2. Experimental

2.1. Materials

The original samples were blast furnace cokes: coke-IAC (Arcelor Mittal, a.s., Ostrava), coke IIOKK, IIIOKK, IVOKK (current OKK Koksovny, a.s., Ostrava; former coking plant Jan Šverma, Ostrava) and the materials with varied carbonaceous structure such as graphite (Fluka), soot (Vulcan 3, Cabot), charcoal (commercial grill wood coal). Potash (K_2CO_3 , 95.5%, Fichema) was used as an additive.

The cokes were produced from coals (USA, Australia) with different content of volatile matter (VM^d) and ash (A^d), as showed in Table 1.

2.2. Techniques

The cokes were crushed, ground in the segmental mill Fritsch 02.102 and fractions below 0.1 mm were used. Coke-IAC was impregnated with 2, 4 and 10 wt. % solution of potash for 30 minutes, and after filtration it was dried at 60°C.

Table 1 Content of volatile matter and ash in studied coal samples

	VM ^d [%]	A ^d [%]
*coalB (coke-IAC)	18.0	4.7
*coalGC (coke-IIOKK)	20.9	8.8
*coalC (coke-IIIOKK)	22.4	6.6
*coalBC4 (coke-IVOKK)	26.7	9.3

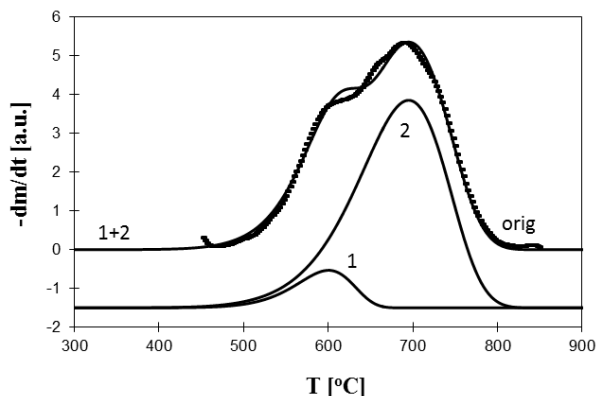
*coalB - Buchanan, Virginia (USA),
 *coalGC - German Creek, Queensland (Australia),
 *coalC - Curragh, Queensland (Australia),
 *coalBC4 - Blue Creek No 4, Alabama (USA)

The other samples were prepared mechanically (in the segmental mill during 1 hour) as blends of 5 wt. % K_2CO_3 and 95 wt. % carbonaceous materials.

Thermal analysis was carried out using simultaneous TG-DSC apparatus Netzsch STA 409 EP. All experiments were conducted under identical conditions: the samples (10-20 mg in weight) were heated up to 1000 °C in the crucibles (aluminum oxide) in a dynamic atmosphere of a dry air (with a flow rate of 100 cm³.min⁻¹) at a heating rate of 10 °C min⁻¹.

3. Results and discussion

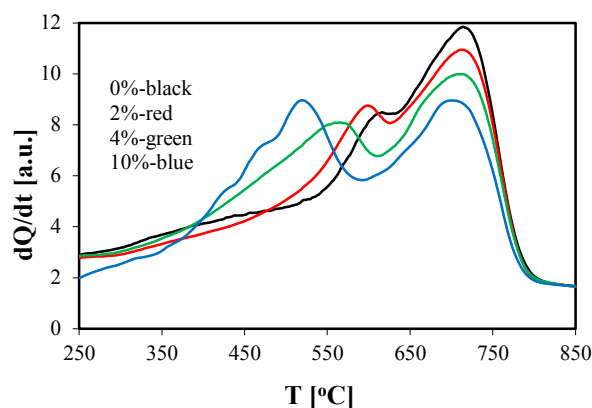
The results obtained from the thermal analysis showed that the coke-IAC thermal oxidation is not a single process, but it proceeds in two partially overlapping stages. This corresponds other authors' findings [17]. It is highly probable that coke contains two carbonaceous structures, a less ordered structure oxidizes at lower temperature, and the more ordered one which is more oxidation-resistant. Fig. 1 (where dm/dt is rate of mass changes) represents the model DTG (derivative of thermogravimetry) curve of the coke-IAC thermal oxidation (curve 1+2) which is distributed into two separate curves corresponding with the oxidation of a less ordered structure of coke-IAC (curve 1) and the oxidation of a more ordered structure (curve 2). Curve marked *orig* indicates experimental curve.

**Fig. 1** Model DTG curves of oxidation of coke-IAC

3.1. The effect of different concentration of K_2CO_3 on the coke oxidation

The catalytic effect of K_2CO_3 on the oxidation of coke-IAC was studied by means of a thermal analysis. It apparent, from the experimental DSC (differential thermal analysis) curves (Fig. 2, where dQ/dt is heat flux difference between sample and standard) of coke-IAC oxidation with potash, that addition of K_2CO_3 influenced mainly the oxidation of the first stage (decrease of temperature of the maximum T_m) while the second stage oxidation went without any changes (comparable values of maximum temperature T_m).

The sample designation *coke-IAC with 0 wt. % solution of K_2CO_3* means impregnation of coke-IAC with pure distilled water. Temperatures T_m (peak maximum on the temperature axis) were determined from DSC curves (Fig. 2, Tab. 2).

**Fig. 2** DSC curves of oxidation of coke-IAC with 0, 2, 4, 10 wt. % solution of K_2CO_3

The effect of K_2CO_3 on the characteristic temperatures is negligible. The temperature of the second maximum T_m is about 700°C for all samples. On the other hand, the influence of potash on the maximum temperature T_m for the first stage oxidation is considerable. With an increasing concentration of additive the maximum temperature T_m shifts towards lower values (Fig. 2, Tab. 2).

The values of apparent kinetic parameters (Tab. 2) were calculated using the method of direct non-linear regression (DNR), which enables determination of apparent kinetic parameters of multistep reactions [16].

The calculation is based on the kinetic Eq. (1).

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (1-\alpha)^n \quad (1)$$

where α is the degree of conversion, t - time (s), T - absolute temperature (K), R - molar gas constant (8.314 J K⁻¹ mol⁻¹), A - frequency factor (s⁻¹), E_a - activation energy (J mol⁻¹) and n is the reaction order.

If the time step is set small enough, the derivatives in Eq. (1) may be replaced by differences [15]:

$$\Delta\alpha = A \exp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \Delta t \quad (2)$$

Assuming the α_0 and t_0 at the beginning of the α vs. t curve, further points of the curve can be calculated from the recurrence relation

$$\alpha_i = \alpha_{i-1} + A \exp\left(-\frac{E_a}{RT_{i-1}}\right)(1-\alpha_{i-1})^n (t_i - t_{i-1}) \quad (3)$$

If the TG curve consists of p various processes with kinetic parameters A_j , E_{aj} and n_j ($j=1$ to p), Eq. (3) can be used for calculation of extent of conversion for individual reactions [15]. In this case, the equation describing the whole curve can express as a sum of particular equations:

$$\alpha_i = \sum_j \alpha_{j,i-1} + \sum_j A \exp\left(-\frac{E_{aj}}{RT_{i-1}}\right)(1-\alpha_{j,i-1})^{n_j} (t_i - t_{i-1}) \quad (4)$$

This equation enables determination of apparent kinetic parameters of multistep reactions by non-linear optimization.

In our calculations we assumed, similarly to other authors, that the coke oxidation is the first-order reaction and that the effect of diffusion can be neglected under used experimental conditions.

Similarly like on characteristic temperatures, potash has an effect on activation energies (Tab. 2).

In the case of the first oxidation stage, an apparent decrease in values occurred. Activation energies E_{a1} fall from 220 kJ mol^{-1} to 80 kJ mol^{-1} with increasing addition of K_2CO_3 (except coke-IAC + 10 wt. % solution of K_2CO_3). The values of activation energy for the second stage E_{a2} stay almost unchanged.

The influence of K_2CO_3 also appeared in connection with reaction heat. The peak areas of DSC curves

are proportional to the values of enthalpy changes. With increasing content of K_2CO_3 , the peak areas increase (Fig. 2).

3.2. The effect of K_2CO_3 on the oxidation of varied carbonaceous structure

In order to assess the effect of K_2CO_3 on the thermal oxidation of variously ordered carbonaceous structures, the following materials were chosen: a fully unorganized structure – soot and charcoal, a partially ordered turbostratic structure – blast furnace coke, and a highly ordered, free-dimensional periodic structure – graphite. The variously ordered carbonaceous structure can be assessed on the basis of maximum temperatures of oxidation T_m using DSC curves (peak maximum on the temperature axis). It can be said that the maximum temperature T_m increases with a more ordered structure (Fig. 3).

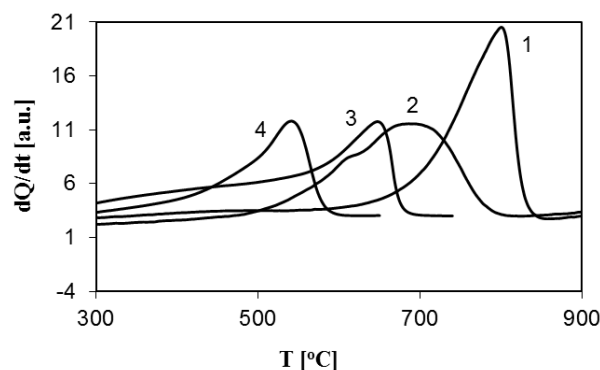


Fig. 3 DSC curves of thermal oxidation of carbonaceous materials (1-graphite, 2- blast furnace coke-IAC, 3-soot, 4-charcoal)

Table 2 Apparent kinetic parameters, temperature of maximum of oxidation of coke-IAC with 0, 2, 4 a 10 wt. % solution of K_2CO_3

	1. stage	2. stage
coke-IAC + 0 wt. % solution of K_2CO_3	$E_{a1} = 220 \text{ [kJ mol}^{-1}]$ $A_1 = 3.259 \times 10^8 \text{ [s}^{-1}]$ $T_{m1} = 616 \text{ [}^\circ\text{C]}$	$E_{a2} = 150 \text{ [kJ mol}^{-1}]$ $A_2 = 1.228 \times 10^{11} \text{ [s}^{-1}]$ $T_{m2} = 714 \text{ [}^\circ\text{C]}$
coke-IAC + 2 wt. % solution of K_2CO_3	$E_{a1} = 170 \text{ [kJ mol}^{-1}]$ $A_1 = 1.820 \times 10^8 \text{ [s}^{-1}]$ $T_{m1} = 599 \text{ [}^\circ\text{C]}$	$E_{a2} = 160 \text{ [kJ mol}^{-1}]$ $A_2 = 1.126 \times 10^6 \text{ [s}^{-1}]$ $T_{m2} = 712 \text{ [}^\circ\text{C]}$
coke-IAC + 4 wt. % solution of K_2CO_3	$E_{a1} = 80 \text{ [kJ mol}^{-1}]$ $A_1 = 3.628 \times 10^2 \text{ [s}^{-1}]$ $T_{m1} = 565 \text{ [}^\circ\text{C]}$	$E_{a2} = 160 \text{ [kJ mol}^{-1}]$ $A_2 = 1.134 \times 10^6 \text{ [s}^{-1}]$ $T_{m2} = 716 \text{ [}^\circ\text{C]}$
coke-IAC + 10 wt. % solution of K_2CO_3	$E_{a1} = 110 \text{ [kJ mol}^{-1}]$ $A_1 = 7.027 \times 10^4 \text{ [s}^{-1}]$ $T_{m1} = 520 \text{ [}^\circ\text{C]}$	$E_{a2} = 160 \text{ [kJ mol}^{-1}]$ $A_2 = 1.211 \times 10^6 \text{ [s}^{-1}]$ $T_{m2} = 701 \text{ [}^\circ\text{C]}$

Next, a thermal analysis of mixtures of carbonaceous materials impregnated with potash (5 wt. %) was performed. Subsequently the values of activation energies (E_{a1} - oxidation of original samples, E_{a1*} - oxidation of carbonaceous materials with K₂CO₃) were determined using direct non-linear regression, Eq. 3 (Tab. 3).

In all cases (except graphite) the addition of potash caused a decrease in activation energies.

Table 3 Activation energy E_a of oxidation of carbonaceous materials

	E_{a1} [kJ mol ⁻¹]	E_{a1*} [kJ mol ⁻¹]	ΔE_a [kJ mol ⁻¹]
graphite	223	223*	0
coke-IAC	94	57*	37
soot	228	186*	42
charcoal	145	96*	49

3.3. The effect of K₂CO₃ on the oxidation of cokes with variant reactivity

In relation to previous experiments, the effect of K₂CO₃ on thermal oxidation of cokes with different reactivity was investigated. Reactivity of coke can be expressed in three ways: as rate constant k of coke reaction with CO₂ or as activation energy E_a at two different temperatures, or as spontaneous oxidation temperature T_{so} (peak maximum on the temperature axis of DSC curve) in air atmosphere.

The reactivity of cokes, which is one of the most important criterion for assessing the quality of coke, is expressed here by the *CRI* index and by the spontaneous oxidation temperature T_{so} , which corresponds with the maximum temperature and their value was determined from DSC curves (Fig. 4a, b). *CRI* values were determined directly in coking plant. The most common method for determining the quality of coke is NSC method [18]: 200 g coke of granulation 19-21 mm reacts with CO₂ at temperature 1100°C for 2 hours. *CRI* Index indicates relative weight loss of coke mass after reaction:

$$CRI = \frac{A - B}{A} \times 100\% \quad (5)$$

A . . . weight of sample before reaction

B . . . weight of sample after reaction

The higher *CRI* and the lower T_{so} , the higher reactivity of coke. Therefore, coke IVOKK is the most reactive, it has the highest *CRI* and the lowest T_{so} (Tab. 4)

Table 4 Values of *CRI* and T_{so} for cokes II-IVOKK

	<i>CRI</i> [%]	T_{so} [°C]	T_{so}^* [°C]
coke-IIOKK	31.6	640	501
coke-IIIOKK	47.0	629	495
coke-IVOKK	56.9	616	490

T_{so}^* - the maximum temperature after addition of K₂CO₃

The addition of K₂CO₃ caused that cokes oxidation occurs in two steps (two peak maximums on the temperature axis, Fig. 4a) unlike original cokes (Fig. 4b).

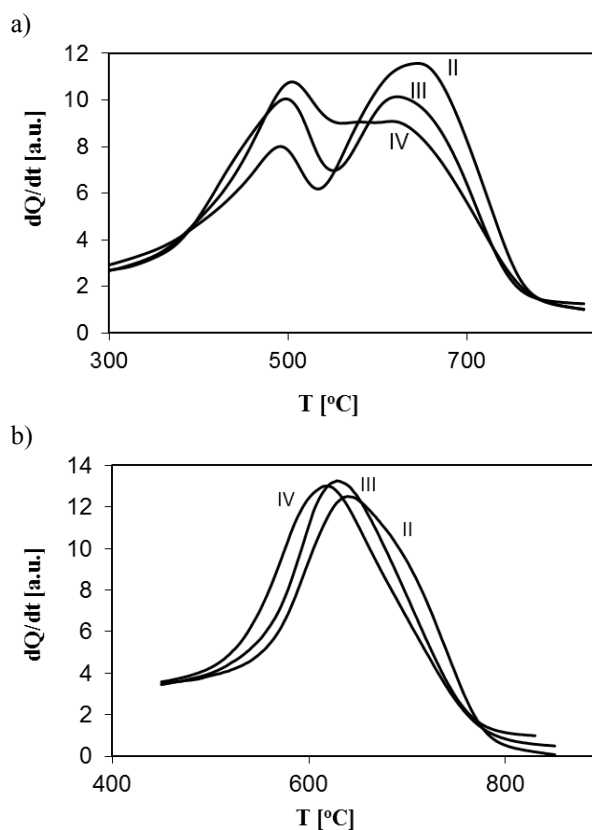


Fig. 4 DSC curves of oxidation of cokes II-IVOKK with 5 wt. % K₂CO₃ (a) and without K₂CO₃ (b)

4. Conclusions

The thermal oxidation of cokes and carbonaceous materials in the presence of K₂CO₃ was investigated by a thermal analysis. The aim of this paper was to give new findings on the effects of K₂CO₃, that could contribute to the understanding of the mechanism of its action and its behavior during coke degradation, what is of considerable technological and economic importance for the blast furnace process. The following results have been obtained:

- the coke thermal oxidation is not a single process, but it occurs in two partially overlapping stages; it is related to two differently ordered carbonaceous structures (Fig. 1)
- the addition of K₂CO₃ influenced mainly oxidation of the less ordered structure while the second stage oxidation occurred without changes (Fig. 2, Fig. 4a)
- the catalytic effect caused a distinct decrease in activation energy (from 220 kJ mol⁻¹ to 80 kJ mol⁻¹), in the temperature of maximum (Tab. 2)
- the effect of potash on the oxidation of carbonaceous materials increases with disorder of their structure: graphite < coke < soot < charcoal (Tab. 3)

- the presence of K_2CO_3 in the mixtures with cokes with different reactivity, indicated by index *CRI* or T_{so} , shifts the spontaneous oxidation temperatures to lower values (Tab. 4, Fig. 4a)

References

1. Kret, J.: Vliv alkálií na výrobu surového železa ve vysoké peci; Hutnické listy 4, 2000, 10.
2. Grigore, M. and Sakurovs, R.: Influence of mineral matter on coke reactivity with carbon dioxide; ISIJ International 46 (4), 2006, 503.
3. Grigore, M. and Sakurovs, R.: Mineral matter in coals and their reactions during coking; Journal of Coal Geology 76 (4), 2008, 301.
4. Gornostayev, S.S. et al.: Behaviour of Coal associated Minerals during Coking and Blast Furnace Processes; Steel Research International 80 (6), 2009, 390.
5. Grigore, M. and Sakurovs, R.: Coke Gasification: The Influence and Behavior of Inherent Catalytic Mineral Matter; Energy and Fuels 23 (7), 2009, 2075.
6. Kim, B.C.: Effect of Thermal Treatment on Coke Reactivity and Catalytic Iron Mineralogy; Energy and Fuels 23 (7), 2009, 3694.
7. Gornostayev, S.S. and Tanskanen, P.A.: An example of alkalization of SiO_2 in a blast furnace coke; Energy and Fuels 21 (5), 2007, 2637.
8. Kaczorowski, J. et al.: The influence of potassium on the Boudouard reaction in manganese production; ISIJ International 47 (11), 2007, 1599.
9. Park, S.W. and Sung, D.H.: Carbonation kinetics of potassium carbonate by carbon dioxide; Journal of Industrial and Engineering Chemistry 12 (4), 2006, 522.
10. Shimomyama, I.: Research Prospect on Coke Reactivity aiming at Low RAR Blast Furnace Operation; ISIJ International 96 (5), 2010, 25.
11. Hilding, T. et al.: Degradation behavior of a high CSR coke in an experimental blast furnace: Effect of carbon structure and alkali reactions; ISIJ International 45 (7), 2005, 1041.
12. Tromp, J.J. et al.: The thermoplasticity of coal and the effect of K_2CO_3 addition in relation to the reactivity of the char in gasification; Fuel 65 (10), 1986, 1450.
13. Kuang, J.P. et al.: Research on alkali-catalyzed gasification of coal black liquor slurry cokes made up by five different coals; Asia-pacific Journal of Chemical Engineering 2 (3), 2007, 152.
14. Zhang, Y.H. and Zou, X.T.: The catalytic activities and thermal stabilities of Li/Na/K carbonates for diesel soot oxidation; Catalysis Communications 8 (5), 2007, 760.
15. Vallova, S. et al.: The influence of selected oxides and carbonates on thermal oxidation of coke; Journal of Thermal Analysis and Calorimetry 71, 2003, 875.
16. Slovak, V.: Determination of kinetic parameters by direct non-linear regression from TG curves; Thermochimica Acta 327, 2001, 175.
17. Zolin, A.: Experimental study of char thermal deactivation; Fuel 81, 2002, 1065.
18. Menéndez, J.A. et al.: Determination of metallurgical coke reactivity at INCAR: NSC and ECE-INCAR reactivity tests; Ironmak. Steelmak. 26, 1999, 117.