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# THE INFLUENCE OF SELECTED OXIDES AND CARBONATES ON THERMAL OXIDATION OF COKE

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## Abstract

An influence of inorganic compounds ($Fe_2O_3$, ZnO, PbO, $CaCO_3$ and $K_2CO_3$) on the blast furnace coke thermal oxidation in the air and in the $CO_2$ atmosphere was investigated by means of thermal analysis. A catalytic effect showed itself at the oxidation in the air, especially with PbO and $K_2CO_3$. These compounds bring the oxidation starting temperature and activation energy down and increase the reaction rate constant most distinctly. The PbO and $K_2CO_3$ actions differ in their mechanisms. $K_2CO_3$ accelerates particularly the amorphous coke fractions oxidation. In the $CO_2$ atmosphere an important catalytic effect occurred only with $K_2CO_3$. The PbO catalytic influence is less distinct.

**Keywords:** coke, kinetics, thermal oxidation, thermogravimetry

## Introduction

An influence of alkalis on the agglomerate quality at agglomeration, on the agglomerate disintegration and on the coke consumption increase at blast furnace process was investigated in practice. When studying the alkalis influence, lime (about 24%), coke (5%) and alkalis ($K_2CO_3$+$Na_2CO_3$ up to 1%) are added to the ore concentrate [1]. Same wastes containing ZnO and PbO besides the iron oxides are treated partly at the agglomeration process.

The main sources of alkalis in the blast furnace process are ores and coke [2]. The alkalis increase the coke oxidation rate in $CO_2$ at a given temperature and shift the oxidation start towards lower temperatures. The coke reactivity increases with the growing alkalis content. It was assumed in [2] that the coke consumption rises due to the reduction of compounds containing Na and K, which results in gaseous metals presence. Then they oxidize again in higher parts of furnace forming carbonates and in this way conditions for the alkalis circulation and their concentration increasing are created.

A correlation between the coke reactivity and ash mineralogical composition is investigated in later works. It was found out that carbonates and chlorides of sodium and

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potassium increase the coke carboxyreactivity [3]. However, if the alkalis are present in the form of clay materials, they have no influence on the coke carboxy reactivity.

When studying the combustion of fly-ash carbon impregnated by alkali carbonates and hydroxides [4], it was found out that the ignition temperature and activation energy decrease.

The aim of the present work was to investigate an influence of inorganic additives ($Fe_2O_3$, $CaCO_3$, ZnO, PbO and $K_2CO_3$) on the coke oxidation kinetics in the air (agglomerate production) and in the $CO_2$ atmosphere (blast furnace process).

## Experimental

### *Materials and techniques*

The original sample was blast furnace coke containing <0.1% $H_2O$ and 14.6% ash. The coke was crushed, ground in the segmental mill, sieved and fractions below 100 μm were used for the measurements. Samples were prepared as a mixture of 5% additives (PbO, ZnO, $Fe_2O_3$, $K_2CO_3$ and $CaCO_3$) and 95% coke and were homogenized in the mill for one hour.

The thermal analysis was carried out using simultaneous TG-DTA apparatus Netzsch STA 409 EP. All the experiments were conducted under the identical conditions: the samples (5 mg in mass) were heated up to 1000°C in the crucibles (aluminum oxide) in a dynamic atmosphere of dry air or $CO_2$ (with the flow rate of 100 $\text{cm}^3\ \text{min}^{-1}$) at the heating rate of 10°C $\text{min}^{-1}$.

### *Determination of apparent kinetic parameters*

The method of direct non-linear regression [5] was used for calculation of apparent kinetic parameters of oxidation processes from thermogravimetric (TG) curves.

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

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E}{RT}\right)(1-\alpha)^{\mathrm{n}} \tag{1}$$

where α is the reaction order.

If the time step is set small enough, the derivatives in Eq. (1) may be replaced by differences. We assume that the TG curve is composed of very small linear segments of the length $\Delta t$, in which the reaction rate is constant:

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

where α is the degree of conversion, $t$ – time (s), $T$ – absolute temperature (K), $R$ – molar gas constant (8.314 $\text{J mol}^{-1}\ \text{K}^{-1}$), $A$ – frequency factor ($\text{s}^{-1}$), $E$ – activation energy ($\text{J mol}^{-1}$) and $n$ is the reaction order.

Assuming the $\alpha_0$ and $t_0$ at the beginning of the α *vs*. $t$ curve, further points of the curve can be calculated from the recurrence relation

$$\alpha_{i}=\alpha_{i-1}+A\exp\left(-\frac{E}{RT_{i-1}}\right)(1-\alpha_{i-1})^{n}(t_{i}-t_{i-1}) \tag{3}$$

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

$$\alpha_{i}=\sum_{j}\alpha_{j,i-1}+\sum_{j}A\exp\left(-\frac{E_{j}}{RT_{i-1}}\right)(1-\alpha_{j,i-1})^{n_j}(t_{i}-t_{i-1}) \tag{4}$$

This equation enables to determine apparent kinetic parameters of multistep reactions by means of non-linear optimization.

In our calculations we assumed, similarly to other authors [4, 6] that the coke oxidation is the first-order reaction and that the effect of diffusion can be neglected under the used experimental conditions.

## Results and discussion

The thermogravimetric experiments showed that only some of the used inorganic compounds have significant influence on the coke thermal oxidation. To compare the effects of inorganic additives, the temperatures of reaction start ($T_i$) were read from TG curves and the apparent kinetic parameters ($E$ and $A$) were determined (Table 1). The calculation

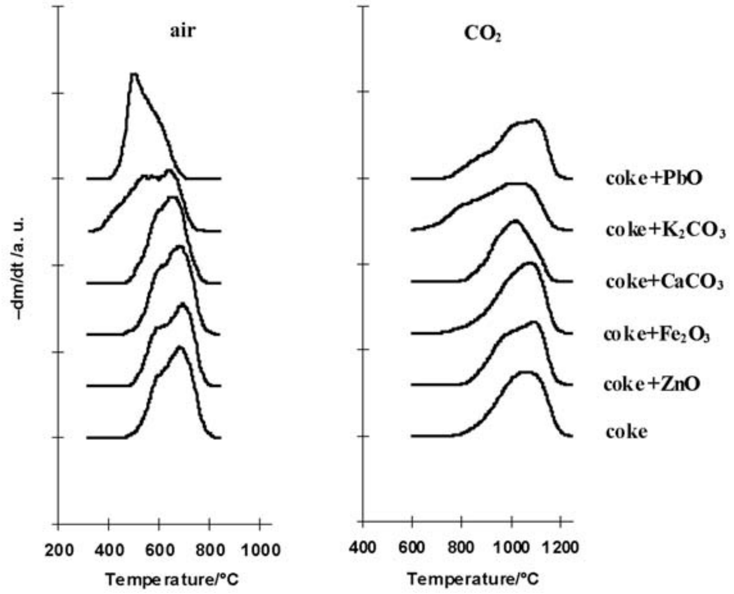

**Fig. 1** DTG curves of oxidation of coke samples in the air and $CO_2$ atmosphere

of kinetic parameters was performed on the assumption that the coke thermal oxidation is not a single process, but it proceeds in two partially overlapped stages. It is in accordance with other authors [7]. The shape of the measured DTG curves of coke oxidation (Fig. 1) also indicates that this assumption is probably correct.

$Fe_2O_3$, $CaCO_3$ and ZnO additions practically did not affect the coke thermal oxidation course neither in air nor in $CO_2$. The $T_i$ temperatures are similar to those for the coke itself. The influence on the process activation energy is not very distinct.

On the contrary, PbO and $K_2CO_3$ showed a strong catalytic effect in the air (Fig. 1).

**Table 1** Temperatures of reaction start and kinetic parameters of coke samples oxidation in the air and $CO_2$

| Sample | $T_i$/°C | 1. stage | | 2. stage | |
|---|---|---|---|---|---|
| | | $E_1$/kJ mol$^{-1}$ | $A_1$/s$^{-1}$ | $E_2$/kJ mol$^{-1}$ | $A_2$/s$^{-1}$ |
| | | air | | | |
| coke | 576 | 217 | $6.02\cdot10^{10}$ | 132 | $4.16\cdot10^{4}$ |
| coke+PbO | 466 | 228 | $1.26\cdot10^{13}$ | 104 | $6.63\cdot10^{3}$ |
| coke+$K_2CO_3$ | 455 | 76 | $2.26\cdot10^{2}$ | 154 | $1.78\cdot10^{6}$ |
| coke+ZnO | 578 | 190 | $1.60\cdot10^{9}$ | 141 | $1.27\cdot10^{5}$ |
| coke+$CaCO_3$ | 555 | 241 | $2.97\cdot10^{12}$ | 118 | $1.14\cdot10^{4}$ |
| coke+$Fe_2O_3$ | 573 | 233 | $6.45\cdot10^{11}$ | 127 | $2.37\cdot10^{4}$ |
| | | $CO_2$ | | | |
| coke | 931 | 210 | $1.06\cdot10^{6}$ | 377 | $6.93\cdot10^{11}$ |
| coke+PbO | 908 | 138 | $7.28\cdot10^{2}$ | 447 | $3.17\cdot10^{14}$ |
| coke+$K_2CO_3$ | 821 | 90 | $1.23\cdot10^{1}$ | 258 | $3.30\cdot10^{7}$ |
| coke+ZnO | 935 | 211 | $1.57\cdot10^{6}$ | 387 | $2.05\cdot10^{12}$ |
| coke+$CaCO_3$ | 916 | 210 | $9.76\cdot10^{5}$ | 522 | $3.19\cdot10^{17}$ |
| coke+$Fe_2O_3$ | 937 | 188 | $1.33\cdot10^{5}$ | 368 | $4.03\cdot10^{11}$ |

Lead monoxide decreases the $T_i$ temperature on the DTG curve by 100°C approximately and the whole process proceeds in a narrower temperature interval comparing with that of the coke itself. These changes, however, are not accompanied by a more distinct change of activation energies.

$K_2CO_3$ shifts the oxidation in the air towards lower temperatures, too and the first stage of the whole process proceeds is the most separate (distinct maximum on the DTG curve at the temperatures of 550°C). At the presence of $K_2CO_3$ a great decrease of the first stage activation energy occurs at the same time.

It can be supposed that the coke itself consists of two carbon structures. Most probably, one of them is a less ordered, more reactive structure (oxidizes sooner, at lower temperatures) and the other is more ordered (less reactive) one. That is why the coke oxidation is not a simple process but proceeds on two stages. They reveal themselves as bifurcation of peaks on the DTG curves (Fig. 1).

Lead monoxide accelerates the oxidation of both coke assumed structures. The whole process is shifted towards lower temperatures. Potassium carbonate catalyses mainly the amorphous carbon mass, while its catalytic effect is not so evident in case of the more ordered structure.

To prove this assumption, a sample of coke with $K_2CO_3$ was annealed 10 min in the air at the temperature of 500°C. At this temperature the oxidation of the assumed less ordered structural form proceeds sufficiently fast. The DTG curves of oxidation of a sample treated in this way as well as of an original sample of coke with $K_2CO_3$ are shown in Fig. 2.

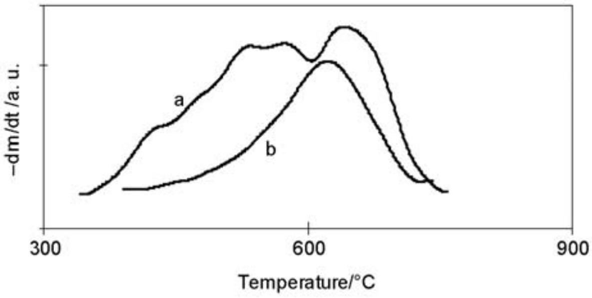

**Fig. 2** DTG curves of oxidation of a – coke+$K_2CO_3$ and b – of the same sample after annealing in the air

It is obvious that the oxidation of the treated sample proceeds as a single process (Fig. 2b). There is only one maximum on the DTG curve corresponding approximately to the second maximum on the DTG curve of the untreated sample (Fig. 2a). We conclude that the amorphous carbon coke structure oxidized when annealing the sample at 500°C and the oxidized structure does not show itself on the DTG curve.

As well as in case of the coke oxidation in the air, $K_2CO_3$ addition has the greatest influence in the $CO_2$ atmosphere. Its presence decreases the oxidation activation energy (both stages) and the temperature of reaction start (Table 1).

The activation energy of the first stage in $CO_2$ atmosphere as well decreases in the presence of PbO. The influence of PbO on the $T_i$ temperature is, however, negligible in this case comparing with its influence during the oxidation in the air.

Differences in the kinetics of coke oxidation in the presence of $K_2CO_3$ and PbO are illustrated by Arrhenius plots (Fig. 3).

The plots show clearly the differences between the effects of PbO and $K_2CO_3$ on the coke oxidation in the air.

The presence of PbO (Fig. 3, lines c) shifts the linear dependency of ln$k$ *vs*. $1/T$ to higher values of rate constant for both stages in comparison with coke itself (Fig. 3, lines a), but the straight line slope is not changed distinctly (minimal changes of activation energies).

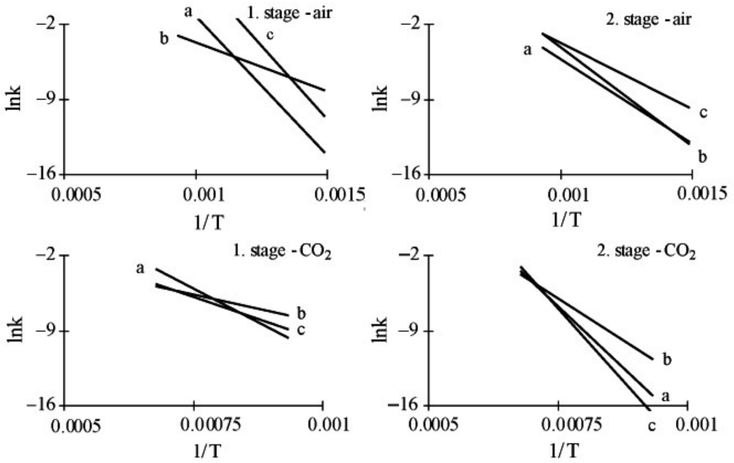

**Fig. 3** Arrhenius plots for oxidation of a – coke, b – coke+$K_2CO_3$ and c – coke+PbO

On the other hand, $K_2CO_3$ addition (Fig. 3, lines b) decreases the activation energy (Arrhenius straight line slope) radically only for the first stage of the coke oxidation in the air and its catalytic effect shows itself particularly in the lower temperature range where the oxidation rate constant is higher by several orders than that for the coke itself (Fig. 3 lines a). This catalytic effect does not appear for the second stage of oxidation of coke with $K_2CO_3$ in the air.

The effect of PbO and $K_2CO_3$ on the oxidation of coke in $CO_2$ atmosphere is less evident. The presence of $K_2CO_3$ slightly decreases the activation energies of both stages of oxidation. The influence of PbO on the coke oxidation in $CO_2$ cannot be simply expressed on the base of our measured and calculated data.

## Conclusions

The results obtained when studying the coke thermal oxidation in the presence of ZnO, PbO, $Fe_2O_3$, $CaCO_3$ and $K_2CO_3$ by means of thermal analysis proved that PbO and $K_2CO_3$ have the most distinct effect on the coke oxidation in the air. But these two substances differ in the catalytic action mechanisms. PbO accelerates the oxidation process as a whole, while $K_2CO_3$ catalyses particularly the less ordered coke structure.

A catalytic effect in the $CO_2$ atmosphere showed itself especially with $K_2CO_3$, while the PbO effect in this atmosphere was not so distinct.

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