

THERMAL OXIDATION OF FINE GRAINED CARBONACEOUS MATERIALS IN THE PRESENCE OF ZN(II), FE(III) AND Pb(II) COMPOUNDS

Vallová S., Slovák V., Leško J.

Department of Chemistry, VSB - Technical University Ostrava, Czech Republic

TERMICKÁ OXIDACE JEMNOZRNNÝCH UHLÍKATÝCH MATERIÁLŮ V PŘÍTOMNOSTI ZN(II), FE(III) A Pb(II) SLOUČENIN

Vallová S., Slovák V., Leško J.

Katedra chemie, VŠB - Technická univerzita Ostrava, Česká republika

Abstrakt

V této práci se sledoval vliv ZnO, PbO, Fe₂O₃ a PbCl₂ na termickou oxidaci vysokopecního koku a grafitu za neizotermních podmínek pomocí termické analýzy. Tímto se modelovaly podmínky pyrometalurgického zpracování směsí vysokopecního a ocelářenského kalu, které obsahují výše zmíněné sloučeniny. Výsledky ukázaly, že přídavek ZnO má zanedbatelný vliv na termickou oxidaci koku a grafitu. Přídavkem Fe₂O₃ došlo ke zvýšení aktivační energie termické oxidace obou materiálů. Nejdůležitější je katalytický účinek olovnatých sloučenin, který způsobil výrazný posun teplotního maxima u grafitu k nižším hodnotám (asi o 300°C). Mimoto, PbO snížil aktivační energii obou sledovaných látek. Proto je dobré vzít v úvahu vliv PbO na oxidaci paliva během pyrometalurgického zpracování v aglomeračním procesu.

Abstract

In the present work the effect of ZnO, PbO, Fe₂O₃ and PbCl₂ on the blast furnace coke and graphite oxidation under nonisothermal conditions was studied by means of thermal analysis. In this way the conditions of pyrometallurgical treatment of blast furnace and steelmaking sludge mixtures containing the above constituents were modelled. The results showed that ZnO addition has a negligible effect on the coke and graphite thermal oxidation. Fe₂O₃ addition results in increasing the thermal oxidation activation energy in both the materials. The most important is the catalytic effect of lead compounds which depress the graphite exothermal maximum temperature considerably (up to 300°C). Moreover, lead (II) oxide depresses the oxidation activation energy of both the studied substances. That is why it will be reasonable to consider the PbO influence on the fuel oxidation in the pyrometallurgical treatment of steelmaking sludge by agglomeration in the open air.

Key words: thermal oxidation, coke, graphite, TG, kinetics

Introduction

Some fine wastes which cannot be recycled directly because of their contents of zinc(II) and lead (II) compounds are produced in the ferrous metallurgy processes. It concerns particularly blast furnace sludge - BFS, basic oxygen furnace sludge - BOFS and electric furnace dust - EFD.

When recycling these wastes in blast furnaces, ZnO and PbO oxides arise and deteriorate the furnace lining. In certain intervals these oxides are liberated in the form of white fumes at tapping of pig-iron, which causes a hygienic harmfulness of the work surroundings and environment. Before the metallurgical processing these wastes have to be treated by hydrometallurgical or pyrometallurgical processes [1] in dependence on the chemical form of zinc and lead. Principal constituents of blast furnace sludge are iron(III) oxide, coke and small amounts of zinc and lead compounds which can be removed by a hydrometallurgical process, e.g. by acid leaching, before the recycling itself. Steelmaking wastes have higher contents (up to tens of per cent) of strong bonded zinc and lead that have to be removed by a pyrometallurgical process, i.e. by thermal reduction. In ref. [2] a possible way of carbothermal reduction of BFS and BOFS mixtures in an inert atmosphere without the necessity to add a reducing agent (coke, coal) is presented. In this work the iron(III) oxide prereluction kinetics under isothermal and nonisothermal conditions in the atmosphere of nitrogen was studied.

The aim of the present work was to study the oxidation of blast furnace coke and graphite at presence of Zn(II), Pb(II) and Fe(III) compounds by means of thermal analysis under nonisothermal conditions. The thermal reduction of BFS + BOFS and/or BFS + EFD mixtures was modelled by additions of oxides to the coke and graphite. PbCl₂ addition modelled the influence of ions sorbed on blast furnace sludge from aqueous solutions.

Experimental

Materials

The original samples were coke (blast furnace coke containing < 0,1 % H₂O and 14,6 % ash) and graphite (Fluka, particle size < 100 μm). The coke was crushed, ground in the segmental mill, sieved and fractions passing 100 μm were used in the measurements. Samples were prepared as a mixture of 5 % oxides (PbO, ZnO, Fe₂O₃) and 95 % coke or graphite. The mixtures were homogenized in the mill for one hour. Other samples were obtained by mixing 20 ml of lead chloride solution in water ($c = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$) with 12 g of the original materials and dried in the air at the room temperature.

Techniques

Thermal analyses were carried out using simultaneous TG - DTA apparatus STA 409 EP/1/F by NETZSCH. All the experiments were performed under the identical conditions: the samples (5 mg in weight) were heated up to 1000°C in the aluminium oxide crucible in the dynamic atmosphere of dry air (with the flow rate of 100 cm³ min⁻¹) at the heating rate of 10 deg min⁻¹. α-Al₂O₃ was used as the reference material.

Determination of apparent kinetic parameters

Coats and Redfern method [3] was used for calculation of apparent kinetic parameters of oxidation processes from thermogravimetric (TG) curves.

The calculation is based on the assumption that the following kinetic equation holds true

(1)

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

In our calculations we assumed, similarly to other authors [4, 5], that the coke and graphite oxidation is the first-order reaction.

After performing an approximate integration of equation (4) according to [3] and arrangement we obtain for $n = 1$

(2)

where T_p is the average temperature in a particular section of the TG curve and β is the heating rate (deg s^{-1}).

Plotting the following dependence

(3)

we obtain a straight line whose slope determines the activation energy E and intercept the frequency factor A .

In the present work we always used the section of thermogravimetric curve (TG) corresponding to the degree of conversion ranging from 0.2 to 0.8 for the kinetic parameters calculation. Since the TG curves are little illustrative and their derivatives (DTG) are calculated, we used the differential thermal analysis curves (DTA) for graphical presentation of results.

Results and Discussion

On the basis of thermogravimetric data the activation energy and frequency factors for all the measured systems were calculated under the assumption of the first-order reaction (Table 1).

Table 1 Temperatures at maximum rate of reaction and apparent kinetic parameters

DTA curves of the coke and its mixtures with the studied oxides are shown in Figure 1.

Fig.1 DTA curves of the coke (1) and its mixtures with ZnO (2), Fe_2O_3 (3) and PbO (4) oxidation

It is obvious from the chart that ZnO and Fe₂O₃ have only minimum influence on the coke oxidation course. The maximum temperature T_m on the DTA curve (Table 1) rests practically unchanged nor the peak shape is influenced by these oxides presence. PbO, on the contrary, changes the process character very dramatically due to its catalytic effect on thermal oxidation. The maximum temperature on the DTA curve is shifted towards lower values by almost 200°C. In addition, the deformed curve shape indicates a significant change in the thermal oxidation mechanism.

The shape of curves 1 - 3 shows evidently that the coke thermal oxidation is composed of several reactions, which makes an exact evaluation of the individual oxide catalytic effect more complicated. That is why this effect was studied on the model system graphite - oxides.

The assessed effect of oxides on the graphite thermal oxidation is shown in Figure 2.

Fig.2 DTA curves of the graphite (1) and its mixtures with ZnO (2), Fe₂O₃ (3) and PbO (4) oxidation

From the standpoint of the DTA curve maximum shift the graphite oxidation is most influenced by PbO presence. The maximum temperature decreased by over 300°C. The graphite DTA curve shape (slope) is changed less, this change is, however, analogous to PbO influence on the coke DTA curve shape. In both the cases the activation energy decrease occurs.

The temperatures corresponding to the maximum coke and graphite rate of oxidation (DTA curve maximums) at PbO presence are almost identical. The assessed values are in good agreement with the maximum temperature ($\approx 500^\circ\text{C}$) for the soot oxidation in PbO presence (DSC, loose contact) [6]. It indicates that the mechanism of PbO influence on the structurally arranged graphite, on the coke with irregular structure as well as on the amorphous soot is similar.

Fe₂O₃ effect can be observed in graphite. This oxide shifts slightly the DTA maximum towards lower values while the process activation energy increases.

ZnO catalytic effect in both studied materials is small and cannot be assessed unambiguously.

PbCl₂ was used to model the graphite oxidation influence of ions sorbed on blast furnace sludge from solution and its effect is obviously seen in Figure 3.

Fig.3 DTA curves of the graphite (1) and PbCl₂ impregnated graphite (2) oxidation

The DTA curve maximum is shifted towards lower values (Table 1) due to this salt effect which is similar to the PbO addition.

However, the coke impregnation by PbCl₂ does not have a significant effect on its oxidation (small T_m decrease and slight activation energy change) and the process as a whole takes place in the same temperature range. It means that the Pb(II) ions sorption on blast furnace sludge from solution will not influence considerably their thermal oxidation in the course of agglomeration process.

Conclusions

The results obtained in the study of the graphite thermal oxidation at presence of ZnO, PbO, Fe₂O₃ and PbCl₂ by means of thermal analysis under nonisothermal conditions showed that graphite is a suitable model system for studying these reactions in blast furnace coke which is the source of carbon substances in blast furnace sludge. Due to the presence of the only graphite structure type the thermoanalytical curves are easy to evaluate and the catalytic effect of various additions can be interpreted unambiguously unlike the coke.

Acknowledgement

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