

## REDUCTION OF LEAD OXIDE BY FINE-GRAINED CARBONACEOUS MATERIALS

As part of the presented work, tests were carried out to check the possibility of replacing of conventional reducers used in the lead pyrometallurgical processes by cheaper, but equally effective substitutes. For research of lead oxide reduction, the following fine-grained carbonaceous materials were used, ie anthracite dust and coal flotation concentrate, as well as traditional used coke breeze for comparison. The obtained test results indicate a similar ability to reduce the lead oxide of all studied carbonaceous materials.

*Keywords:* lead oxide, lead, fine-grained carbonaceous materials, anthracite dust, coal flotation concentrate, reduction, thermogravimetry

### 1. Introduction

Depletion of natural resources of metals encourages producers from the metallurgical industry to put special emphasis on processes aimed at using metals from secondary raw materials in the production. Their use is also supported by the economic aspect. Production of metals from recyclable materials is always less expensive than using primary sources, i.e. metal ores. An example of a metal whose production in the world from secondary sources has long ago surpassed the production from primary raw materials is lead, where the processing of used batteries plays a decisive role [1-3]. In Poland, processing of used batteries, next to the ISP process (Imperial Smelting Process) – simultaneous production of zinc and lead from Zn-Pb concentrates derived from the ores enrichment processes, is in fact the only source of lead directed to refining processes.

One of the fractions processed in the processing of battery scrap to obtain lead is a battery paste, which one of the main components is lead oxide. Traditionally, in the pyrometallurgical processes of lead production, fuels / reducers in the form of coke or coke breeze are used. Due to their high and constantly rising prices, it is justified to look for cheaper alternative fuels / reducers [4-7] used, among others, in the mentioned processes. In the paper tests to check the possibility of replacing in the pyrometallurgical processes of obtaining lead of conventional reducers with cheaper but equally effective substitutes were carried out. For research on the reduction of lead oxide, fine-grained carbonaceous materials were used, ie anthracite dust, coal flotation concentrate and for comparison coke breeze.

### 2. Research methodology

In the research of carbonaceous materials gasification and the lead oxide reduction process, the Netzsch thermal analyzer, model STA 449 F3 Jupiter, was used. The device was equipped with carriers that allow for thermogravimetric (TG) and differential thermal analysis (DTA) measurements. The scheme of the device is shown in Fig. 1, and the basic operating parameters are shown in Table 1.

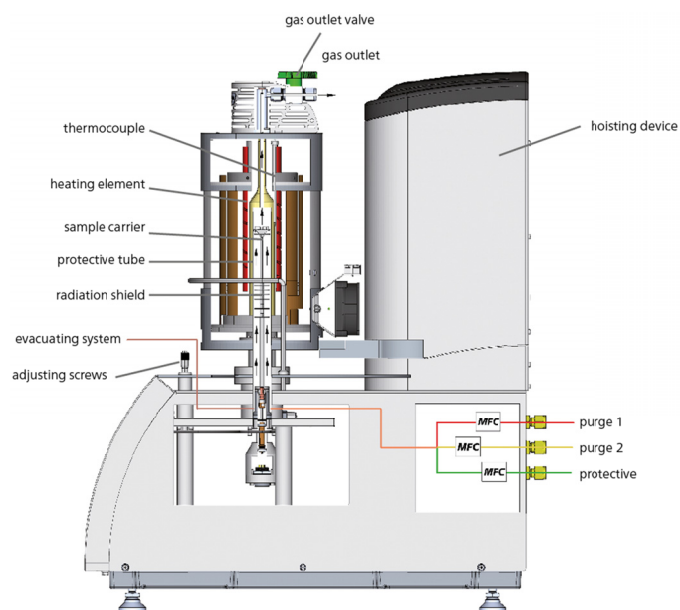


Fig. 1. Schematic of the STA 449 F3 Jupiter thermal analyzer

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TABLE 1

Basic parameters of the STA 449 F3 Jupiter thermal analyzer

<b>Work temperature</b>	<b>-150÷2000°C</b>
<b>Working atmosphere</b>	Air, N <sub>2</sub> , CO, CO <sub>2</sub> , Ar, He, H <sub>2</sub> , gas mixtures
<b>Maximum weight</b>	35 g
<b>Measurement accuracy</b>	1 µg
<b>Heating speed</b>	od 0.001°C/min. do 50°C/min.
<b>Available measurements</b>	TG, DTA

In the thermogravimetric studies carried out as part of the work, the adopted sample heating program consisted of three main stages (Fig. 2):

- heating the sample at the rate of 20°C/min. to the selected temperature value,
- isothermal heating of the sample at this temperature for a period of 30 minutes,
- cooling the sample to 800°C at the rate of 20°C/min.

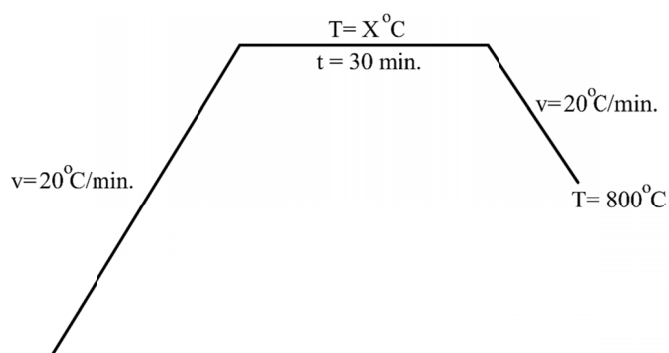


Fig. 2. Temperature diagram of the lead compounds reduction process

In order to determine the impact of the material form on the speed of the reduction process, the tests included measurements for the material in a powder and agglomerated form. The temperature of 900, 925, 950, 975 and 1000°C was assumed as the isothermal stand temperatures of powder samples during TG analysis. Research for agglomerates was carried out at temperatures of 900 and 1000°C. A 10% addition of carbonaceous material was used. The gasification of carbonaceous materials was carried out at a temperature of 1000°C.

In the case of powder samples, they were placed in a DTA/TG crucible made of Al<sub>2</sub>O<sub>3</sub>, which was then placed on the carrier in the analyzer working chamber (Fig. 3). For samples prepared as agglomerates, a special type of Al<sub>2</sub>O<sub>3</sub> crucible in the form of an open saucer was used, on which the sample was placed centrally (Fig. 4).

All measurements of the reduction process took place in a gas mixture consisting of:

- synthetic air – injected into the furnace chamber through two inputs with a total flow of 100 ml/min,
- argon with a purity of 99.999% – used as the so-called protective gas passing through the weight part of the device and then entering the working chamber.

The gasification of carbonaceous materials was conducted in the atmosphere of argon.

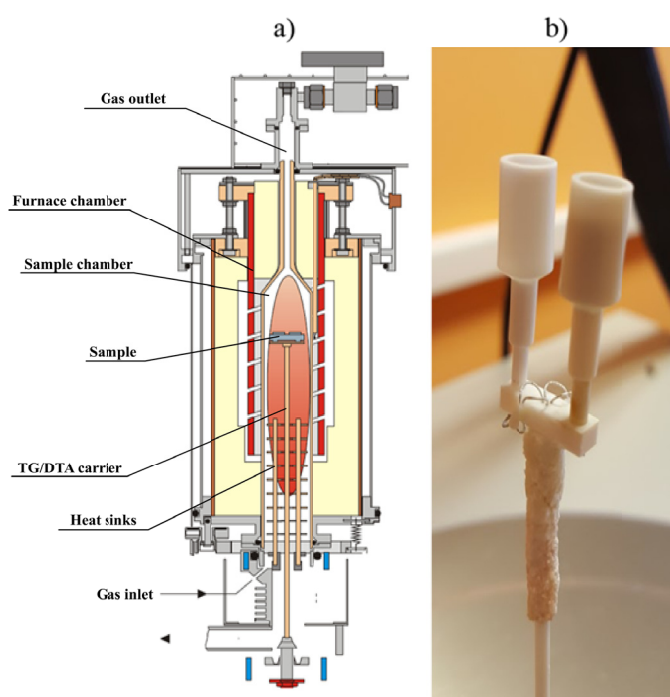
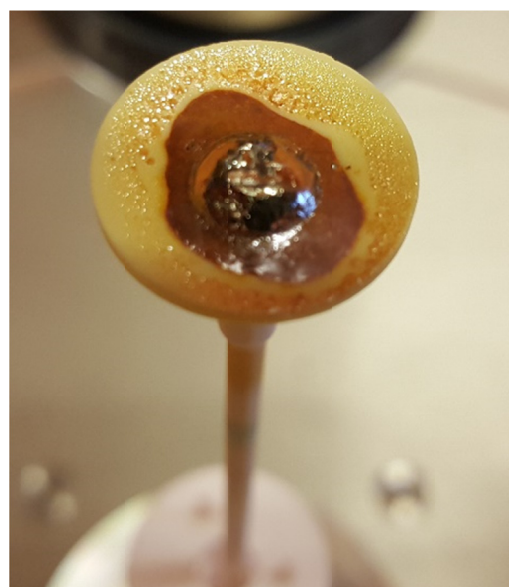
Fig. 3. The method of placing the sample in the device: a) diagram of the thermal analyzer working chamber, b) Al<sub>2</sub>O<sub>3</sub> crucible

Fig. 4. Crucible in the form of an open saucer

### 3. Results and discussion

Thermogravimetric curves obtained during the gasification process of carbonaceous materials at a temperature of 1000°C are presented at Fig. 5. In the case of coke breeze and anthracite dust, only a small loss of samples mass was observed (about 5%), whereas in the case of coal flotation concentrate it reached about 90%. It can be assumed that the observed mass changes were associated with the removal of moisture and volatile parts from carbonaceous materials. Such a large weight loss in the case of the latter material is mainly related to the release of hydrocarbons

under the influence of temperature. The analysis of waste gas from the coal flotation concentrate gasification process carried out with Gasmeter™ DX4000 from Gasmeter Technologies Inc. showed the presence of, among others, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>6</sub>H<sub>14</sub> and CHO<sub>2</sub>.

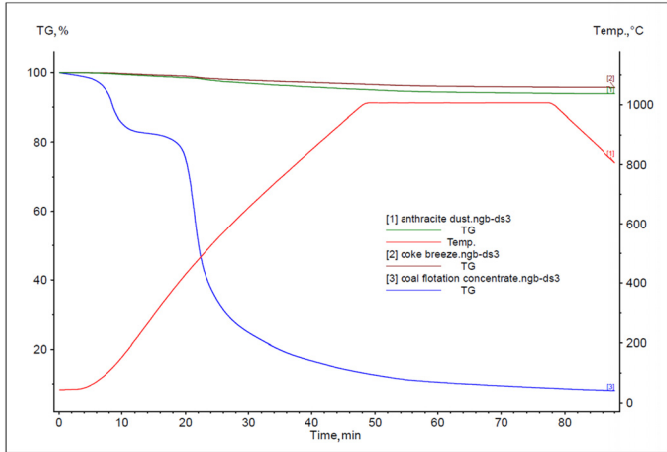
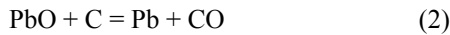


Fig. 6. Thermogravimetric curves obtained during gasification processes of carbonaceous materials

In the case of reduction of lead oxide with a solid carbon reducer, following reactions may take place:



The changes in the free enthalpy  $\Delta G^0_T$  of these reactions, determined on the base of thermodynamic data from the HSC program [8], are shown in Fig. 6.

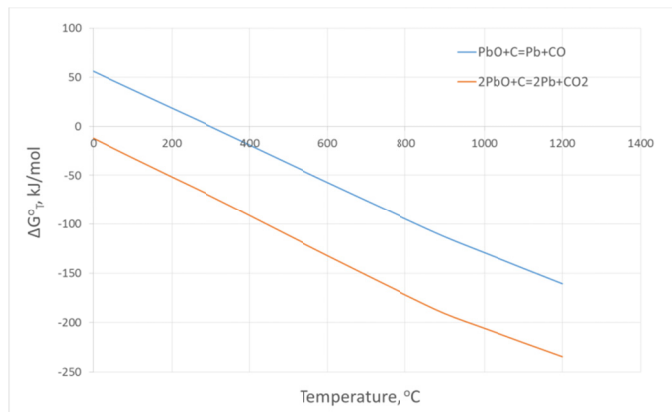


Fig. 6. Change of the free enthalpy  $\Delta G^0_T$  of the PbO reduction reaction with carbon

As the results from the above data for the 600÷1200°C temperature range,  $\Delta G^0_T$  values for both reduction reactions assume values below -50 kJ/mol, which indicates that from the thermodynamic point of view, reaction (1) and (2) could proceed to the right.

If there is a reduction reaction occurring with oxygen access (reactions characteristic for many metal oxide reduction

processes in metallurgical aggregates), the coal reducer gasifies according to total and incomplete combustion, i.e.



Reactions (2) and (4) are also accompanied by the reaction of Boudouard, which product is carbon monoxide – the basic reducer in metallurgical processes. Fig. 7 presents the values of the free enthalpy change  $\Delta G^0_T$  of the mentioned reactions, also determined on the base of the thermodynamic data from the HSC program [8].

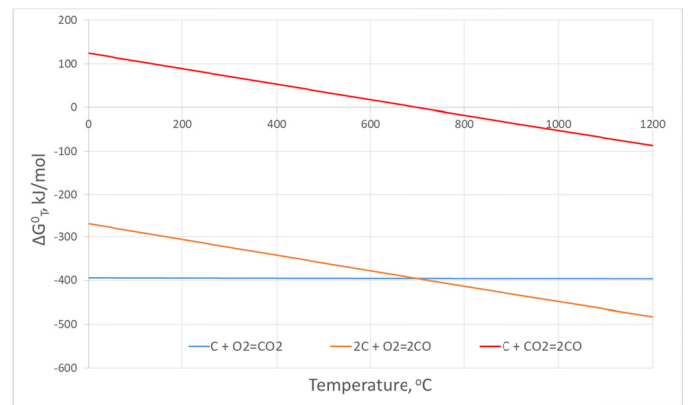
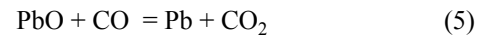


Fig. 7. Change of free enthalpy  $\Delta G^0_T$  of coal combustion reaction and Boudouard reaction

The reduction experiments were carried out in the atmosphere of air, thus apart from direct reduction, there could be a reaction using CO as a reducing agent.



The determined changes in the free enthalpy of reaction (5) are shown at Fig. 8 [8].

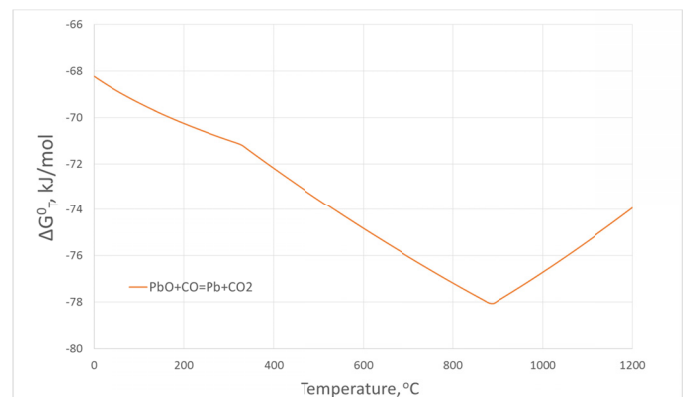


Fig. 8. Change of free enthalpy  $\Delta G^0_T$  of PbO reduction reaction with carbon monoxide

Also in the case of this reaction it appears that under the conditions of experiments from the thermodynamic point of view it is possible to reduce lead oxide with the use of carbon monoxide. It should be mentioned that in the case of coal flotation

concentrate, a number of hydrocarbons will also participate in the reduction reactions. The comparison of the curves obtained as a result of thermogravimetric studies for the reduction of lead oxide with use of anthracite dust (samples in a powder form), are illustrated at Fig. 9. Based on their analysis, two areas of different mass losses of the tested samples were identified during their heating. An example of a thermogravimetric curve recorded at 900°C is shown at Fig. 10. In the first stage, for all analyzed samples there was a rapid loss of sample mass associated with the reduction of PbO and the release of carbon dioxide. After the reduction process, reoxidation of the samples was observed. This effect occurred regardless of the process temperature and ranged from 1 to 2% of the sample weight. It can be assumed that this was the case in the absence of a coal in the sample, and thus carbon monoxide in the atmosphere.

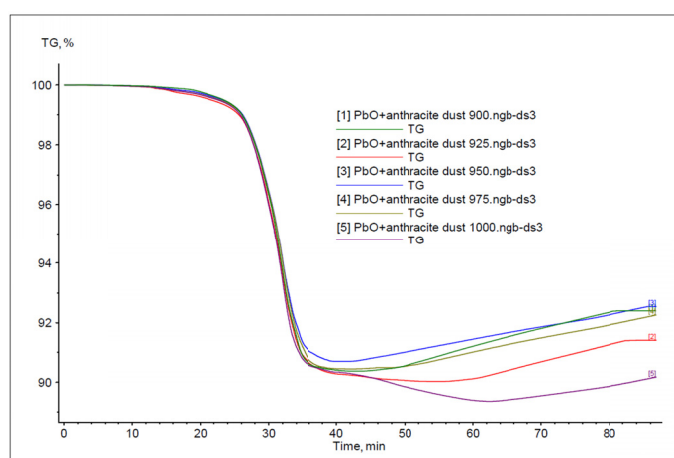


Fig. 9. The comparison of thermogravimetric curves of PbO reduction by using anthracite dust (samples in powder form)

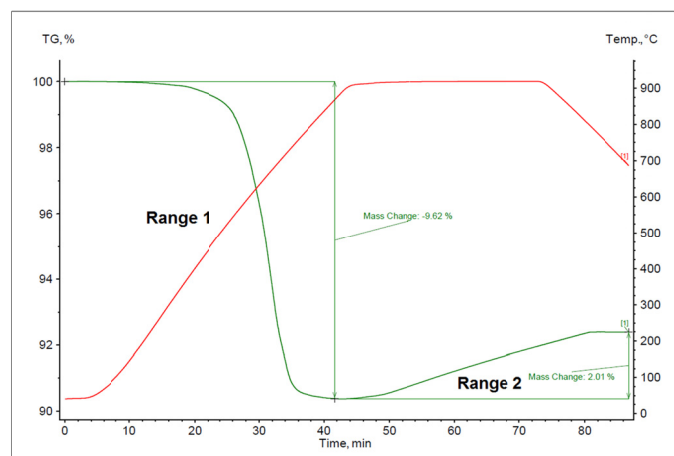


Fig. 10. Thermogravimetric curve of PbO reduction by using anthracite dust at 900°C (samples in powder form)

In the case of the PbO reduction process using the coal flotation concentrate (Fig. 11), it was found that regardless of the temperature, the oxide reduction takes place gradually. This is evidenced by the bends on the TG curve (Fig. 12) and the consequent abrupt mass losses. The initial loss of mass during all

measurements was related to evaporation of moisture from the material and was from 0.16 to 0.39% of the sample mass. In the case of curves recorded at the two highest measurement temperatures, ie 975 and 1000°C, in the final stage of the measurement, a slight increase in the mass of both samples was found, amounting about 0.05% of the mass. This effect, similar to the reduction with anthracite dust, was associated with surface reoxidation of the lead. All curves obtained, regardless of the temperature of the measurement, show a very similar course and shape.

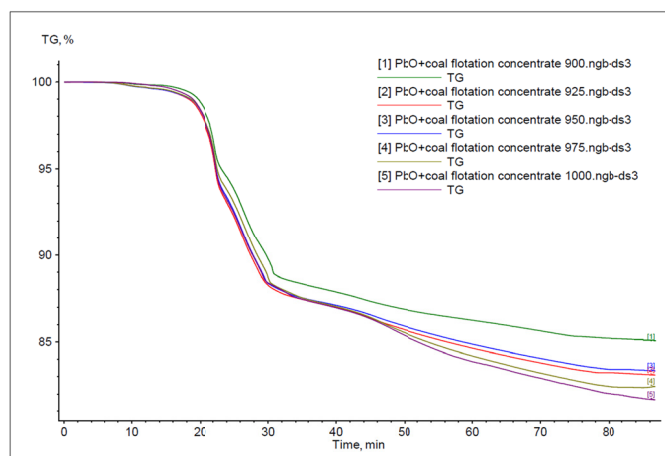


Fig. 11 The comparison of thermogravimetric curves of PbO reduction by using coal flotation concentrate (samples in powder form)

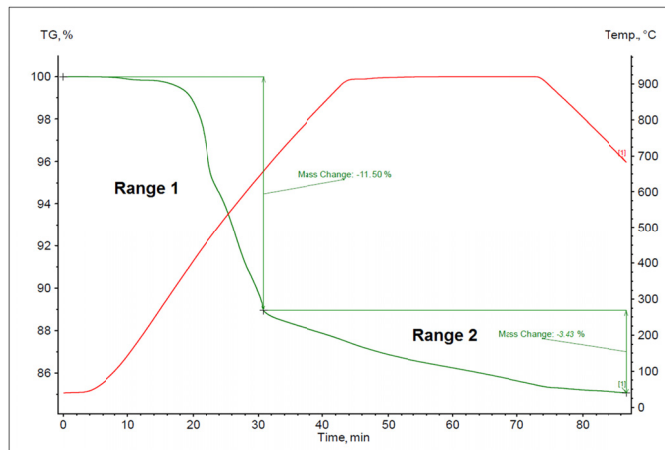


Fig. 12. Thermogravimetric curve of PbO reduction by using coal flotation concentrate at 900°C (samples in powder form)

The use of coke breeze as a reducer in the analyzed process does not significantly affect the character of the thermogravimetric curves (Fig. 13). Regardless of the temperature adopted, all recorded thermogravimetric curves had the same characteristic course and practically very slightly differed in individual mass losses.

Fig. 14-19 presents a comparison of the obtained PbO reduction curves using individual materials in the form of an agglomerate. For comparison, curves for powder materials were also applied. On the basis of the analysis of thermogravimetric curves, it was found that only in the case of samples containing anthracite dust

(at 900°C) there is a clear effect of the form in which the material was situated (Fig. 14). The use of the material in the form of agglomerate influenced the change of the course of the TG

curve at the final stage of the process. This change may have been caused by the reduced susceptibility of the sample to reoxidation. In the case of all other TG curves, there was no significant

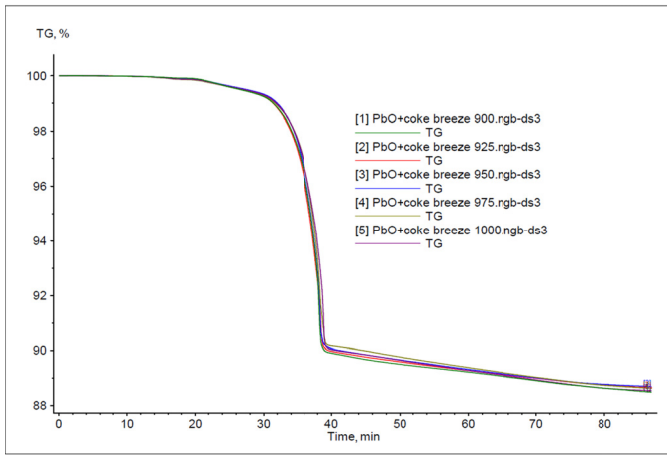


Fig. 13. The comparison of thermogravimetric curves of PbO reduction by using coke breeze (samples in powder form)

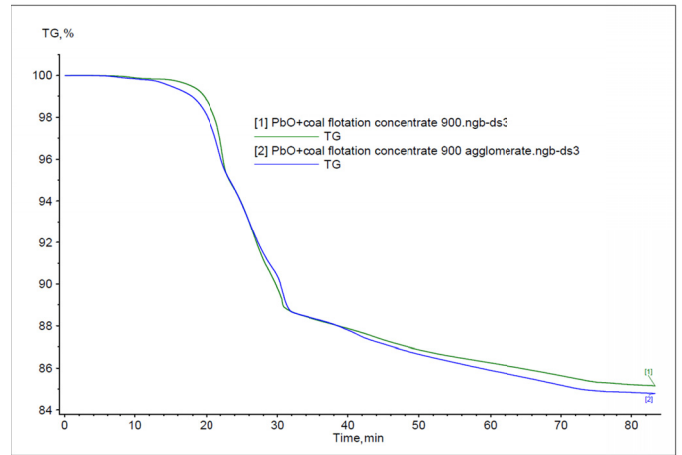


Fig. 16. Comparison of thermogravimetric curves of PbO reduction at 900°C, by using coal flotation concentrate (sample in powder form and agglomerate)

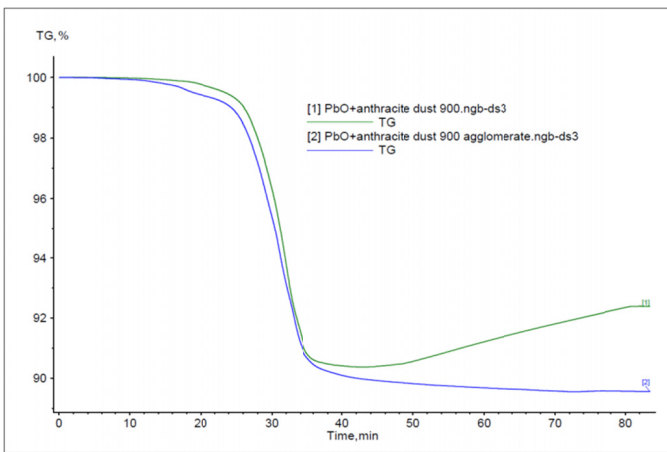


Fig. 14. Comparison of thermogravimetric curves of PbO reduction at 900°C, by using anthracite dust (sample in powder form and agglomerate)

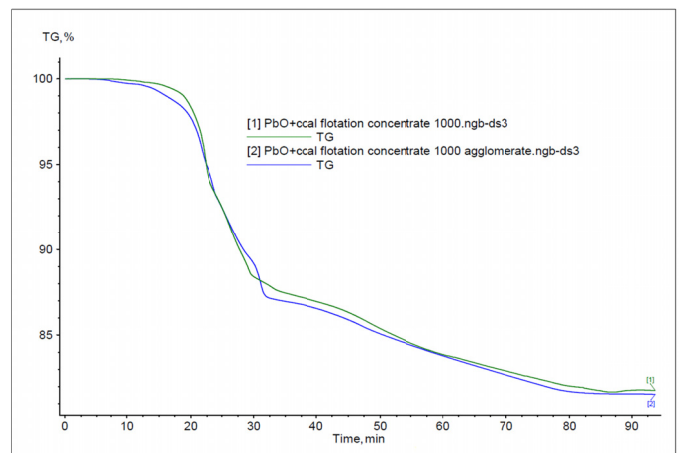


Fig. 17. Comparison of thermogravimetric curves of PbO reduction at 1000°C, by using coal flotation concentrate (sample in powder form and agglomerate)

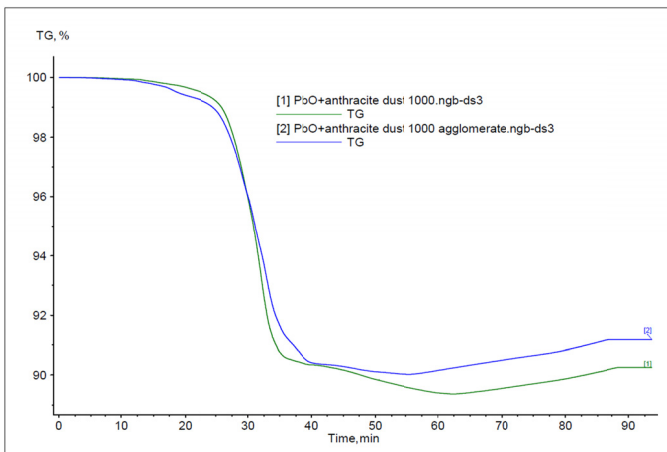


Fig. 15. Comparison of thermogravimetric curves of PbO reduction at 1000°C, by using anthracite dust (sample in powder form and agglomerate)

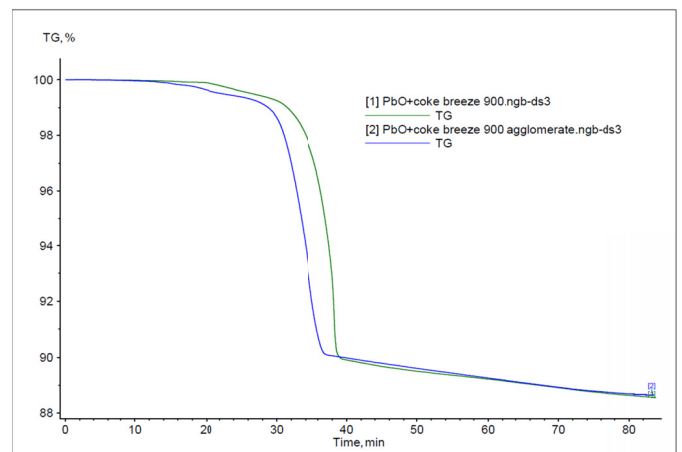


Fig. 18. Comparison of thermogravimetric curves of PbO reduction at 900°C, by using coke breeze (sample in powder form and agglomerate)

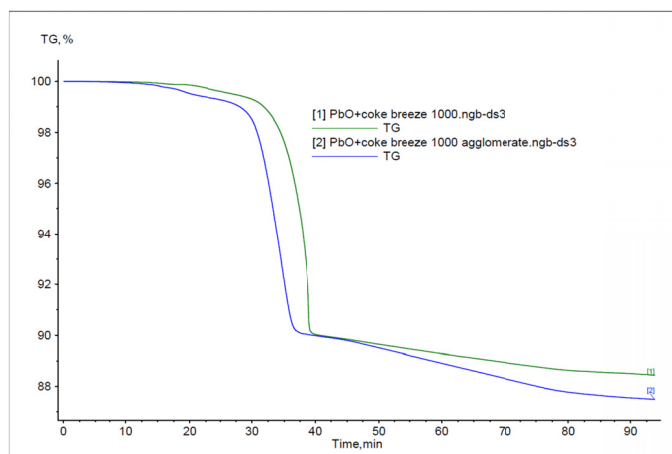


Fig. 19. Comparison of thermogravimetric curves of PbO reduction at 1000°C, by using coke breeze (sample in powder form and agglomerate)

influence of the material form. The recorded differences in the mass of samples between the respective curves did not exceed 1% (Table 2).

#### 4. Summary

Thermogravimetric tests of lead oxide reduction using coke breeze (traditionally used as a reducer in industrial processes of battery paste processing) and also alternative, cheaper carbonaceous materials, ie anthracite dust and coal flotation concentrate, showed in all cases a similar course of TG curves obtained during the processes. The character of the thermogravimetric curves for all the reducers used does not change as the temperature increases. In all cases, two ranges can be found that clearly differ in the speed of mass loss. Tests carried out using material in an agglomerated form showed no significant influence of the form of the material introduced to the process on the character of TG curves. The obtained test results indicate a similar ability to reduce lead oxide of all studied carbonaceous materials, therefore on their basis it can be assumed that both anthracite dust and coal flotation concentrate can be used as replacements for commonly used coke breeze.

TABELA 2

Changes in the mass of samples during PbO reduction (samples in powder form and agglomerate)

Substrates	Sample form	Temperature, °C	Total mass change, %
PbO + anthracite dust	powder	900	-7,60
	agglomerate		-9,83
	powder	1000	-9,74
	agglomerate		-8,17
PbO + coal flotation concentrate	powder	900	-14,83
	agglomerate		-14,99
	powder	1000	-18,09
	agglomerate		-18,16
PbO + coke breeze	powder	900	-11,51
	agglomerate		-10,78
	powder	1000	-11,60
	agglomerate		-11,85

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