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THERMOANALYTICAL INVESTIGATIONS OF SOME INDUSTRIAL WASTES PRODUCED IN STEEL WORKS

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The experiments involves three types of industrial wastes produced by iron works, which create serious hazards to the natural environment: (1) paint-shop sludge, (2) oil-polluted diatomite, and (3) oil-polluted scale. The choice of an appropriate and safe storage method should be based on extensive physicochemical examination.

DTA, in combination with other data, allows characterization of the combustible properties of wastes. Thermoanalytical measurements were carried out in a dynamic air atmosphere. Enthalpy values were calculated from peak areas of DTA curves. Thermoanalytical data were compared with calorimetric results obtained with an oxygen bomb.

The production processes in steel works result in the generation of over a hundred types of wastes, which differ widely in their physical and chemical properties. These properties are of fundamental interest in searching for effective waste management procedures [1]. Differential thermal analysis (DTA), which has frequently been used to characterize sewage sludges [2–5], is not applied for the routine examination of industrial wastes. Zeman et al. [6] utilized DTA to investigate the pyrolysis of municipal refuse. Bartoszewski [7] presented the TG–DTG–DTA diagrams of some major industrial wastes, and emphasized the possibility of applying DTA for the investigation of industrial waste materials.

Experimental

The experiments involved some steel works wastes: (A) paint-shop wastes, (B) oil-polluted diatomite, and (C) quenching tank scale. The physicochemical compositions of the samples were determined by standard methods. DTA was carried out with an OD–102 derivatograph (MOM, Budapest). All experiments were conducted under identical conditions: 306 to 538 mg samples were heated up to 1273 K in platinum crucibles in an air atmosphere at a heating rate of

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10 deg min^{-1}, the reference material being α-Al_2O_3. The standards recommended by the Standardization Committee of ICTA [8] were applied for calibration of the apparatus. Heats of reaction (ΔH_{DTA}) were calculated by the Simpson method of numerical integration of DTA curves. The heats of combustion (ΔH_{comb}) were determined in a KL–5 bomb calorimeter (Precyzja, Poland).

Results and discussion

The physicochemical compositions and thermal degradations of the investigated wastes are shown in Table 1 and Fig. 1, respectively. The thermal decompositions proceed in several steps, at different rates and with different weight losses. The reactions are completed at 1023 K, and with weight losses at this temperature of 49.5%, 35.0% and 26.8% for wastes A, B and C, respectively. For wastes A and C, the weight losses are almost identical to those on heating at 823 K. Only in the case of waste B does the duration of the heating process have a distinct influence on the volume of volatile materials produced.

Despite the differences in the physicochemical compositions, the natures of the curves are very similar for the three wastes under study. The broad exothermic processes observed between 403 and 1023 K are primarily associated with degradation of the organic components. The small rise in the DTA curve above

Table 1 Physicochemical compositions of wastes

Waste	A	B	C
Weight loss at 378 K (%)	10.5	4.9	3.3
Weight loss at 823 K (%)	48.9	47.9	30.0
SiO_2 + particles insoluble in strong acids (% dry solids)	21.6	57.4	54.8
Metals: (% dry solids)			
Na	0.19	0.11	0.43
K	1.03	0.54	0.67
Ca	1.11	0.06	0.17
Mg	0.61	0.27	0.27
Fe	7.01	1.43	6.91
Pb	1.08	n.d.	n.d.
Zn	5.72	0.01	0.21
Ni	0.02	trace	0.03
Cu	0.04	n.d.	0.23
Cr	3.10	n.d.	0.02
Mn	0.06	0.02	0.09
Cd	0.01	n.d.	n.d.

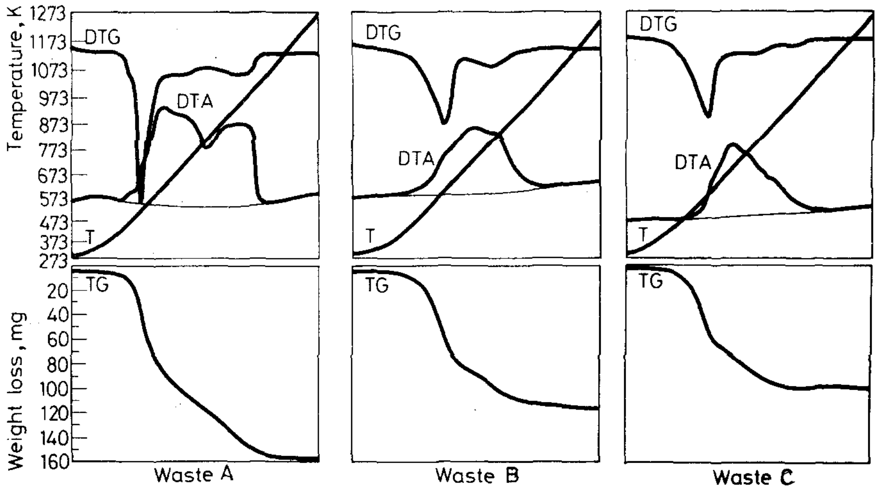

Fig 1 Thermoanalytical curves of wastes A, B and C

1073 K for each of the samples may be attributed to the formation of Fe_2O_3 and the conversion of γ-Fe_2O_3 to α-Fe_2O_3 [9].

The thermal effects calculated from the peak areas of the DTA curves and the measured calorific values are listed in Table 2.

As shown by these data, the calculated heat effects of the decomposition reactions are lower than those measured in the bomb calorimeter for every sample. There seem to be two major factors that may account for the differences between the calculated and measured values: more intensive oxidation of the wastes and of the primary oxidation products in the bomb, and the escape of volatile reaction products from the open system of the derivatograph. Compared to the data reported on the pyrolysis of polymers [10], the differences in the ΔH_{DTA} and $\Delta H_{comb.}$ values obtained in our study are significantly smaller. For polymers, the $\Delta H_{comb.}/\Delta H_{DTA}$ values ranged between 10.6 and 87.9.

Table 2 Results of enthalpy measurements

Waste	Oxygen bomb $\Delta H_{comb.}$, $kJ \cdot g^{-1}$	DTA ΔH_{DTA}, $kJ \cdot g^{-1}$	$\frac{\Delta H_{comb.}}{\Delta H_{DTA}}$
A	15.07	9.40	1.60
B	12.49	4.88	2.56
C	9.45	4.02	2.38

The data sets obtained in this experimental study seem to corroborate the existence of a correlation between ΔH_{DTA} and $\Delta H_{comb.}$. Nevertheless, the number of experiments is too small to allow a determination of the correlation coefficients. However, taking into account the inhomogeneity of the samples, it is worthwhile to make use of the DTA curves (and of the data obtained via this route) for analytical investigations of industrial wastes. There are two further advantages of applying DTA: the preparation of samples is very easy, and the duration of the measuring procedure is relatively short.

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Zusammenfassung — Drei Arten industrieller Abfälle eines Stahlwerks, die schwere Umweltbelastungen darstellen, wurden untersucht: (1) Lackiererei-Schlamm, (2) ölhaltiger Diatomit, (3) ölhaltiger Kesselstein. Geeignete sichere Deponien setzen ausführliche physikalisch-chemische Untersuchungen voraus. DTA in Kombination mit anderen Untersuchungen erlaubt die Charakterisierung der Verbrennungseigenschaften der Abfälle. Die thermoanalytischen Untersuchungen erfolgten im Luftstrom, die Verbrennungswärmen wurden aus den DTA-peak-Flächen berechnet. Die Ergebnisse werden mit denen kalorimetrischer Messungen in einer Sauerstoffbombe verglichen.

Резюме — Проведены эксперименты с тремя видами промышленных отходов чугунно-литейных предприятий, представляющих серьезную опасность для окружающей среды. Среди них были шлам красильных цехов, загрязненная маслом инфузорная земля и загрязненная маслом железная окалина. Выбор уместного и безопасного способа их хранения должен быть основан, исходя из их обширного физико-химического исследования. Метод ДТА в комбинации с другими методами дает возможность охарактеризовать топливные свойства таких отходов. Термоаналитические измерения были проведены в динамической атмосфере воздуха. Значения энтальпии были вычислены из площадей пиков кривых ДТА. Термоаналитические данные были сопоставлены с калориметрическими, полученными в кислородной бомбе.