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REPORT ON THE WORKSHOP: POTENTIAL OF NON-TRADITIONAL THERMAL ANALYSIS METHODS

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ABSTRACT

During the workshop with 47 participants, the state-of-the-art of several non-traditional techniques of thermal analysis was presented and the possibilities of these methods were discussed.

Status reports on emanation thermal analysis, thermosonimetry and thermomagnetometry were given by Prof. V. Balek (Czechoslovakia), Dr. K. Lønvik (Norway) and Prof. S.St.J. Warne (Australia), respectively, followed by progress reports and discussion contributions.

The possibilities of EMF measurements for the investigation of alkali metal halides were outlined by Prof. H.J. Seifert (F.R.G.), the use of low- and high-power microwave energy was reported by Prof. J. Karmazsin (France) and Dr. J. Rouquerol (France) discussed the possibilities of so-called inverse thermal analysis.

In this workshop report, the status reports and progress reports are presented, followed by notes and discussion contributions.

INTRODUCTION

New and sensitive methods for the investigation of solid substances are needed, mainly for checking the quality of raw materials, intermediate products and final products in the production of materials with defined properties and for the optimization of the associated technological procedures. Magnetic, electric and other properties of solids are usually measured under dynamic conditions of thermal treatment. Methods indicating changes in the structure of the defect state of solids are of special importance, as structure defects substantially affect the reactivity, sinterability and other properties of solid materials.

In recent years some techniques based on non-traditional principles have been developed. By the use of such and of new methods of data evaluation we can often obtain new information about solids.

Thermal Analysis Highlights, 8th ICTA, Bratislava, Czechoslovakia.

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This was the reason why the organizers of the 8th International Conference on Thermal Analysis reserved a part of the scientific programme to non-traditional methods and why they organized a panel discussion on these topics, so that many of the participants could become acquainted with these techniques and discuss with the authors the possibilities of their application. These contacts during the Conference gave the authors the chance to obtain new ideas for their future work.

EMANATION THERMAL ANALYSIS: A STATUS REPORT

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ABSTRACT

A status report on emanation thermal analysis in the workshop on less-common methods is given. The methods of sample labelling, the principles of the technique and possible applications are outlined.

INTRODUCTION

Emanation thermal analysis is by definition [1] “a technique in which the release of radioactive inert gases from substances is measured as a function of temperature or time whilst the substances are subjected to a controlled temperature programme”.

Inert gases are used as indicators of the state of solids and their changes. Inert gas atoms do not react with a solid in which they were incorporated in trace amounts before the measurements and are released from the solid by diffusion or by recoil of the inert gas atoms. The inert gas atoms gain recoil energy (of the order of 85 keV per atom) during their formation by nuclear reactions, e.g., by radioactive decay.

Sample labelling

In most instances, it is necessary to label the solids to be studied in order to allow the subsequent measurement of the gas release from the samples. Various methods can be used for labelling of samples. The classical emanation technique [2] uses the natural radioactive gases, radon isotopes (historically called emanation). In this labelling technique, the parent isotopes (e.g., ^{228}Th or ^{224}Ra) of the inert gas (^{220}Rn) are coprecipitated in trace amounts from the solution during the preparation of the solid. When it is impossible to introduce the parent isotopes during the course of preparation, the sample to be measured is impregnated with a solution containing ^{228}Th and ^{224}Ra nuclides. ^{220}Rn is formed in the substance as a consequence of alpha decay, according to

$$^{228}\mathrm{Th} \overset{\alpha}{\rightarrow} {}^{224}\mathrm{Ra} \overset{\alpha}{\rightarrow} {}^{220}\mathrm{Rn} \overset{\alpha}{\rightarrow} \qquad (1)$$

Other nuclear reactions, such as beta decay, (n, α) and (n, p), can be used for the production of inert gases by irradiation of solids [3]. Argon and krypton can be produced in this way, e.g., in alkali or alkaline metal earth halides. Nuclear fission reactions have also been used for the incorporation of the radionuclides ^{133}Xe and ^{85m}Kr into solids [4,5].

Ion bombardment [6] by accelerated inert gas ions can be used for labelling a wide variety of solids, in both the surface and volume of the sample. Various radioactive and non-radioactive isotopes of inert gases have been used for sample labelling; the concentration profile of the incorporated inert gas is dependent on the energy of the inert gas ions and also on the structure and composition of the solids.

Another fairly universal technique of sample labelling consists in the diffusion of inert gases into solids at high temperature and pressure [7,8]. Various labelling techniques applicable with emanation thermal analysis were reviewed by Balek [8].

Trapping and mobility of inert gases in solids

The solubility of inert gas atoms (Kr, Xe and Rn) in solids is small; the inert gases incorporated into solids are situated in substituting or interstitial positions in the lattice, and the inert gas atoms are trapped at the lattice defects such as vacancy clusters, dislocations, grain boundaries and pores. In solids with a layer structure the gas atoms may be situated in the space between the layers; some solids possessing this structure form clathrates.

The mobility of the inert gases is strongly dependent on the structure of solids and its defects. An important role in gas migration is played by impurities of various kinds and natural or artificially induced defects (e.g., by mechanical treatment or irradiation).

The defects in the solid can serve both as traps and as diffusion paths for the inert gas. A survey of the influence of various factors on the migration of inert gases in solids is given in refs. 8 and 9. In instances when inert gas atoms were incorporated directly into solids, diffusion mechanisms control the release of the inert gases from the solids. When no structural or phase changes take place in the solid, random walk diffusion is assumed to occur. Forced diffusion is considered in instances of structural or phase changes in the solids.

When the inert gas atoms are created from their parents by nuclear reactions within the solids, the recoil mechanism of inert gas release should be taken into account in addition to the diffusion. The recoil plays an especially important role at temperatures where the diffusion of the inert gas in the solids is negligible, and also with solids of large surface area.

Theoretical concepts according to Flügge and Zimens [10], Zaborenko and Kapustin [11], Beckman [12], Carter [13], Redhead [14], Kelly and Matzke [15], Norgett and Lidiard [16] and Kříž and Balek [17–19] can be used for evaluating experimental data from emanation thermal analysis. A survey of the theories of inert gas release from solids has been given by Balek [8,9]. Recent developments of ETA theory applicable to the study of dispersed solids during non-isothermal heating are outlined in the contributions to this workshop.

Equipment for ETA

The equipment produced [20] by Netzsch (Selb, F.R.G.) for the measurement of radioactive inert gases released from solids permits the measurement of trace amounts of inert gases which are carried from the sample being studied to the radioactivity detector by a carrier gas. This carrier gas, of controlled chemical composition, humidity, flow-rate, etc., can usually also be applied as the gaseous medium for the sample.

ETA equipment gives the possibility of simultaneous measurement using other methods of thermal analysis such as DTA, TG/DTG, dilatometry and evolved gas analysis.

Radiation safety of ETA measurements

The biological hazards of the radioactive inert gases used for the labelling of solids should be mentioned. The labelling of the samples is performed in a glove-box certified for work with radioactive nuclides. Versatile equipment for the labelling of finely crystalline or powdered samples by the impregnation technique is available from Netzsch. For those who are interested, labelling of samples can be organized by Netzsch and the labelled samples delivered to the customer.

The installation of ETA equipment and the measurements can be performed in any chemical or physical laboratory equipped with an exhaust. As trace amounts of inert gases are used for the labelling and 10–100 mg samples are used for one measurement, the radioactive inert gas, after dilution by the carrier gas, does not represent a biological hazard.

Potential of the application of ETA

By means of emanation thermal analysis, information about solids and the processes taking place in these solids and solid surfaces can be obtained.

The following properties of solids and the processes taking place in them can be investigated by means of ETA:

- surface, morphology and microporosity of dispersed and porous solids,
- defect state of the structure of both crystalline and amorphous solids,
- annealing of structure defects, crystallization, recrystallization and sintering,
- chemical reactions in solids and on their surfaces, including solid–gas, solid–liquid and solid–solid interactions.

The following parameters that characterize quantitatively the solid-state changes were suggested on the basis of theoretical models by various workers [16–19]:

- internal and external surface area,
- defects of solids,
- radon diffusion coefficient in pores and the corresponding activation energy of diffusion,
- inert gas diffusion coefficient in the solid matrix and the corresponding activation energy of diffusion,
- kinetic constants of the annealing of structure defects, recrystallization, sintering and other processes evaluated from inert gas release data under isothermal or non-isothermal conditions.

Activation energies of inert gas diffusion, representing the mobility of inert gases in solids and their transport properties, have been evaluated for a number of solids, including metals, alkali and alkaline earth metal halides, oxides and carbides. The stability of radiation and other non-equilibrium defects in crystalline solids has been assessed using inert gas release patterns. This new experimental technique has been called [21] thermodiffusion spectroscopy of defects.

The temperature intervals of the surface and defect state changes and of phase changes and chemical transformations have been determined and new insights into the respective processes were obtained using ETA experimental data. For example, the existence of metastable phases of the thermal decomposition of solids and changes in the concentration of structure defects in the pre-melting period of crystalline solids were revealed by ETA.

The results of emanation thermal analysis are often compared with those obtained by other methods, such as surface area measurements, X-ray diffraction, DTA, thermogravimetry and dilatometry. The equipment for simultaneous measurements by ETA, DTA, TG, DTG or dilatometry available from Netzsch ensures the optimal conditions for direct comparison of the results.

Emanation thermal analysis makes it possible, in contrast to X-ray diffraction patterns, to investigate poorly crystalline or amorphous solids. In contrast to adsorption measurements for surface area determination, ETA permits the investigation of the surface continuously, even at elevated temperatures during heat treatment of solid samples, without the necessity to interrupt the heat treatment and to cool the sample to liquid nitrogen temperature. For this reason, ETA may reflect the surface quality at elevated temperatures more accurately than adsorption measurements.

In contrast to DTA and thermogravimetry, emanation thermal analysis makes it possible to investigate processes that are not accompanied by thermal effects or mass changes. ETA permits the study of the sintering of powdered or gel samples, which would be difficult by means of dilatometry.

Moreover, by applying different radioactive labelling of either the surface alone or the volume of the grains, the processes taking place in the surface and in the bulk of the sample have been discerned by ETA.

To assist in the wider application of emanation thermal analysis in various fields of materials science and in physico-chemical research, we can highlight the following aspects of ETA application:

(i) The choice of an appropriate technique of sample labelling. Parent nuclides of inert gases (e.g., ^{228}Th, ^{224}Ra or ^{222}Ra) are used for labelling solids when a relatively permanent source of inert gas atoms is required in the solid, e.g., when investigating phase changes, sintering or solid-state reactions in the course of heating to high temperatures, changes in the microstructure of cement suspensions during hydration or changes in the microporosity and defect state of solids in general. The direct incorporation of inert gases by ion bombardment is used when thermal annealing of structure defects (induced by irradiation) or processes in the surface layers of solids are investigated.

(ii) The choice of the appropriate experimental conditions (heating, cooling rate, gas medium, etc.), with respect to the aim of the measurements and the subsequent evaluation of experimental data.

(iii) Appropriate ETA measurements and acquisition and treatment of the experimental data. When computers are used, the "true" forms of experimental curves are directly reconstructed, taking into account the inertia of the apparatus [22].

(iv) Evaluation of experimental data, using appropriate theoretical models; assessment of the properties of solids and evaluation of kinetic parameters of a solid-state process. Reconstruction of defective solid media.

Examples of applications of ETA

Determination of the transport properties and the defect state of solids

Inert gas diffusion parameters evaluated from ETA measurements reflect the mobility of inert gases in solids, which can be used for the determination of the defect state of solids.

The differences in the mobility of neon, argon, krypton and xenon ions in a tungsten single crystal were demonstrated by Kornelsen and Sinha [23]. The spectra of the xenon released from three different faces of a tungsten single crystal after 400 eV Xe bombardment are demonstrated in Fig. 1. It

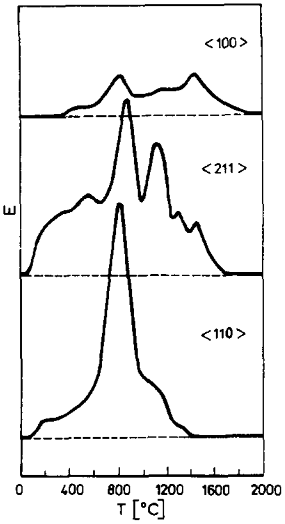

Fig. 1. ETA curves of xenon release from three different faces of a tungsten single crystal, heated at a constant heating rate of 10°C min^{-1}. Xenon was introduced into the sample by ion bombardment, using an energy of 400 eV.

was shown [23–25] that the mobility of Xe and Kr in W, SiO_2, CaF_2 and other single crystals differs according to the crystallographic directions of the single crystals. It is believed that the effect of channelling plays an important role here and in the distribution profile of inert gas atoms introduced by ion bombardment. The diffusion of radon in various metals, such as Mo, W and Fe, measured at elevated temperatures made possible the determination of the temperature of lattice loosening [26], called the Tamman temperature.

The diffusion of inert gases in polymers [27,28] can be used for the characterization of the permeability of polymer membranes. The diffusion properties of some organic solids and polymers have been determined using ETA measurements [29,30].

The ETA curves of Ba salts of phthalic, isophthalic and terephthalic acids [31] showed differences in solids composed of molecules exhibiting positional isomerism. A progressively increasing emanation release rate for Ba salts of long-chain monocarboxylic fatty acids has been reported [32].

It was shown [33] that the presence of impurities in a rutile lattice, such as Al^{3+}, Fe^{3+}, Zn^{2+} and residual SO_4^{2-} ions, strongly influences the perfectness of the rutile structure and its defect state. The activation energy of radon diffusion was used to indicate the changes in the defect concentrations caused by the presence of impurities and by heat treatment of rutile in air and nitrogen.

The influence of the thermal and chemical history on the active state of powdered iron(III) oxide was assessed from values of the activation energy

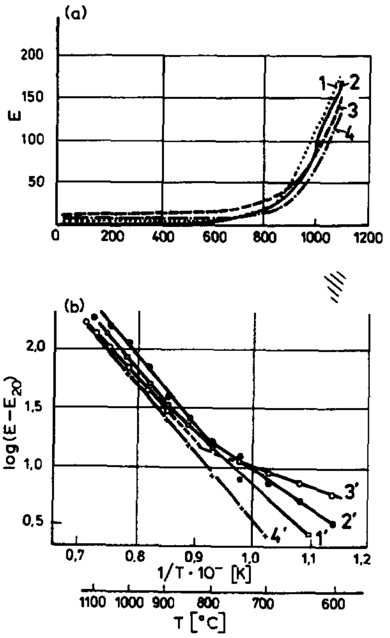

Fig. 2. (a) ETA curves of iron(III) oxide powders prepared by heating various iron salts to 1100°C in air: (1) iron(II) carbonate; (2) iron(II) sulphate; (3) Mohr's salt; (4) iron(II) oxalate. Dependence of E on temperature; heating rate, 10°C min^{-1}. (b) $\mathrm{Log}(E - E_{20})$ versus $1/T$ obtained from the experimental data in (a).

of radon diffusion, determined the experimental results of ETA at temperatures below 0.5 T_m, where T_m is the melting point in the absolute Kelvin scale [34]. In this temperature range the activation energy of radon diffusion reflects the concentration and type of non-equilibrium defects remaining in the structure of iron(III) oxide after the decomposition of initial iron salts used for the preparation of the oxide samples. Hüttig [35] and Hedvall [36] called this phenomenon the structure memory of solids.

The annealing of structure defects, affecting the active state of solids, has been studied. The decrease in the activity is indicated by an increase in the activation energy of radon diffusion [34].

Figure 2 shows log E_D versus $1/T$ for iron(III) oxide samples prepared from four different iron salts by heating at temperatures up to 1100°C in air. The values of the energies of radon diffusion in the temperature range 600–750°C, $Q = 46$, 79, 117 and 126 kcal mol^{-1}, correspond to iron oxide samples prepared by heating Mohr's salt, iron sulphate, iron carbonate and iron oxalate, respectively. The highest values, corresponding to iron(III) oxide from the oxalate, indicated the lowest activity of the solid [34].

Changes in surface and morphology of solids

The changes taking place in the surface and morphology of powdered and gel solids have been investigated by means of ETA.

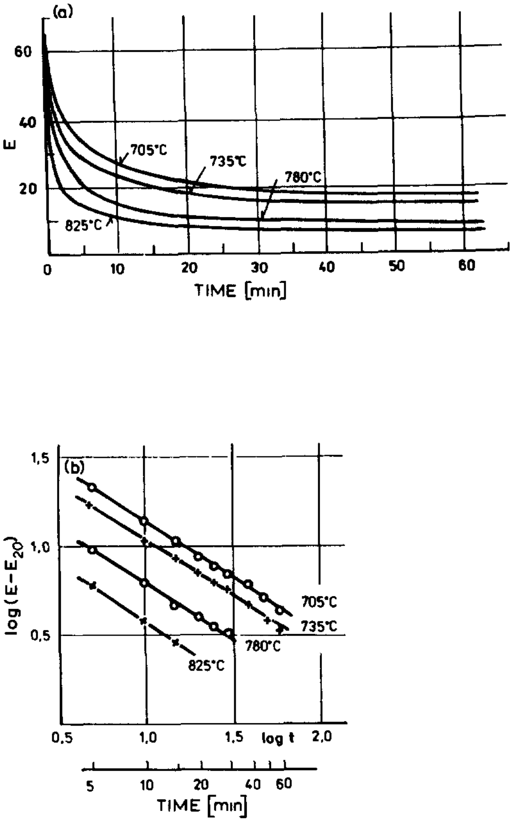

Fig. 3. ETA curves of thoria powder (from the hydroxide) during isothermal heating in air at 705, 735, 780 and 825 °C. (a) E versus time. (b) Log $(E - E_{20})$ versus log(time).

It was shown during investigations of the sintering of finely dispersed Cu, NiO, MgO, Fe_2O_3, ThO_2 and other solids that ETA is a powerful tool for the study of sintering, especially in its initial stage [26,37–39]. A comparison between the ETA data and those obtained by traditional adsorption measurements on finely dispersed solids is discussed later. Gel materials such as silica gel, xerogels of urania, titania and other materials prepared by the so-called "sol–gel" technique, were advantageously investigated by ETA directly during their drying, recrystallization or sintering. Differences in the behaviour of the urania xerogels caused by various concentrations of gelation additives, various means of drying, by ageing, etc., have been determined by ETA [40].

The kinetic parameters for iron(III) oxide and thorium oxide sintering were evaluated on the basis of ETA experiments. Figure 3 shows the ETA isothermal curves for initial sintering of thorium oxide in the range 660–825 °C.

The results obtained obey the kinetic law

$$\log S_{\text{eff}} = n \log t + \text{constant} \tag{2}$$

where $n = 0.64$ and S_{eff} is the surface area reflected by the radon diffusion in the respective temperature range. Assessment of the sinterability of dispersed samples based on ETA was suggested [39] and recommended for industrial laboratories.

Structure transformations

ETA was used by a number of workers [41–48] to study the changes in structure taking place during heating and cooling of solids. During systematic investigations of KNO_3, $NaNO_3$, PbI_2 and other salts it was shown that the temperature intervals of phase transitions of the first and second order (from the thermodynamic viewpoint) may be determined by ETA.

The differences between the surface and volume stages of crystallization and melting were demonstrated on ETA curves. The crystallization and melting of glasses [46–48] in PbO–SiO_2 and Ge–Se–Te systems was studied by ETA.

Dehydration and thermal decomposition of salts and hydroxides

Numerous studies using ETA for the study of the thermal decomposition and concentration of hydroxides, carbonates, oxalates, nitrates, sulphates, iodates and other salts have been reported in bibliographies by Zimens and Freyer [49] and Zimens and Mieckeley [50], in a review by Balek [8] and in a book by Balek and Tölgyessy [9].

The existence of metastable phases appearing immediately after the decomposition of solids was revealed and their thermal stability characterized by ETA. Moreover, ETA was used for the assessment of the active stage of solids prepared by the decomposition of various salts and hydroxides.

The use of ETA in the construction of phase diagrams in KCl–$CaCl_2$, CaO–Fe_2O_3, $NaBeF_3$–$NaPO_3$, $NaBeF_3$–KPO_3 and pyrophosphoric acid–carbamide systems [51–53] should be mentioned. The application of ETA is most advantageous for determining the phase diagrams of poorly crystalline or glass-like systems, where traditional methods do not provide satisfactory results in the determination of phase change temperatures.

Solid-state reactions

Solid–gas reactions. The reaction kinetics of the reaction $NiO + H_2 = Ni + H_2O$ was investigated by means of ETA, using ^{222}Rn for NiO labelling [54]. During heating of NiO in hydrogen, a peak appears on the ETA curve between 230 and 300 °C. A similar peak of water release was simultaneously recorded by a catharometer.

The application of ETA is especially advantageous for studying gas–solid reactions with industrial gases such as hydrocarbons, where the gaseous products of the reactions can hardly be detected. Various gas–solid reactions have been investigated by ETA from the viewpoint of chemical kinetics and reaction mechanism; one of the most important reactions is the oxidation of metals. The surface oxidation of metallic copper labelled by ^{85}Kr was studied by Chleck and Cucchiara [55] and the reaction rate, reaction order, concentration and temperature dependence were determined. It was shown that oxidation during friction wear can be assessed by comparing ^{85}Kr losses in air and in an inert atmosphere.

Matzke [56] used ^{133}Xe release measurements to establish the temperature dependence of the growth of oxide layers on stainless steel, Ti, Ni, Cu and alpha-brass, 40 kV Xe ion bombardment being used for labelling the metals.

A special kind of solid–gas reaction is catalytic reactions taking place on solid surfaces. Catalytic reactions on ZrO_2 and MgO surfaces were investigated by means of ETA by Zhabrova et al. [57]. The catalytic reaction and the subsequent regeneration of the catalyst are accompanied by inert gas release. The reaction of hydrogen–oxygen mixtures on platinum foil labelled by ^{222}Rn was studied by Jech [58].

ETA measurements carried out by Beckman and Teplyakov [59], in the course of various catalytic reactions on Al_2O_3, supported theoretical considerations about the selectivity of the active centres in the surface of the catalysts.

Solid–liquid reactions. The hydration reactions of tricalcium silicate and various cements [60–62] with water vapour present in air and also in the liquid phase were investigated by ETA.

ETA was used for the study of solid–gas and solid–liquid reactions involved in corrosion. Radioactively labelled surfaces are sensitive to all chemical influences that cause changes in the surface of a crystalline lattice. Current methods used to evaluate anti-corrosive or protective agents are generally unreliable, and in many instances take several months to complete. ETA measurements make it possible to carry out such investigations relatively quickly and simply. Corrosion of glasses, building materials and metals imperceptible to the human eye can be demonstrated [63–68] within a few minutes or hours. This method is suitable primarily for relative measurements or for comparisons of various substances using a comparative scale.

Figure 4 shows ETA results obtained during the hydration of Portland cement (PC-400) in water ($w/c = 0.3$) under isothermal conditions at 35, 45 and 65 °C. The reactivity of the cement towards water can be determined by ETA in the early stage of the interaction. Moreover, the changes of surface and morphology taking place in the hydration products of cement have also been investigated by this method.

For tricalcium silicate, the effects on hydration influenced by the activa-

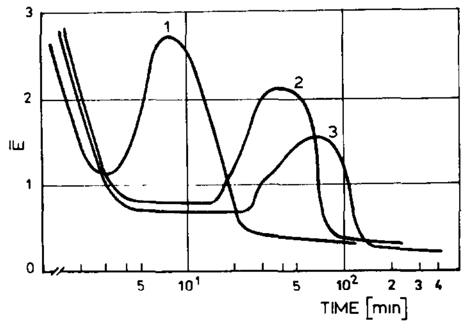

Fig. 4. ETA curves of Portland cement–water suspension (w : c = 0.3) measured during isothermal heating at (3) 35, (2) 45 and (1) 65°C.

tion of the solid by heating and subsequent cooling and by the presence of various admixtures were investigated [60]. For cement hydration [69], ETA results obtained at different temperatures were compared with consistometric and calorimetric measurements. ETA was used successfully in the study of surface hydration [67] where calorimetric and consistometric measurements were not sensitive enough.

It should be pointed out that ETA permits the investigation of changes in the microstructure of a cement paste, i.e., when the size of the micropores is comparable to the size of radon atoms, $d = 0.4$ nm. Good agreement between ETA results and adsorption measurements was found. ETA was suggested [61] as a method suitable for the characterization of the reactivity of cement under various technological conditions.

Solid–solid reactions. A number of reactions between solid powders, e.g., $ZnO–Fe_2O_3$, $ZnO–Al_2O_3$, $UO_2–ZrO_2–CaO$, $TiO–BaCO_3$ and $CaO–SiO_2$, have been studied by means of ETA [68–73]. A systematic study of the $ZnO–Fe_2O_3$ system demonstrated that ETA can be used advantageously for the investigation of the initial stage of the reaction, the bulk reaction and the formation of the structure of the ferrites. DTA, dilatometry and X-ray diffraction were not sensitive enough to indicate the initial reaction stage. The high sensitivity of ETA towards reaction between powders permitted the determination of the reactivities of the components of the reaction mixtures. The reactivities of iron(III) oxide samples with various chemical and thermal histories, determined by ETA [74], agreed well with the results of other experimental techniques.

Moreover, ETA revealed differences in the reactivities of commercial iron(III) oxide samples considered to be identical by traditional surface area measurements [75]. The difference in the reactivities was checked during heat treatment of a reaction mixture corresponding to the technological conditions of ferrite manufacture [76]. The ETA results in Fig. 5 enabled a distinction to be made in the behaviours of two commercial samples of

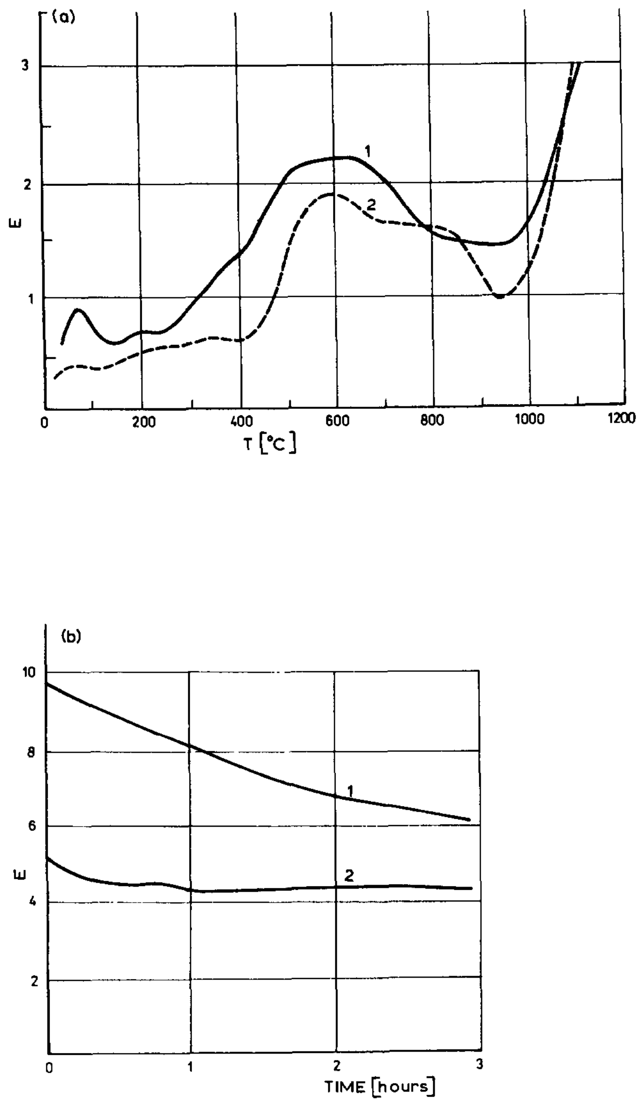

Fig. 5. ETA curves of $ZnO + Fe_2O_3$ (1 : 1) reaction mixtures. The ZnO was labelled with ^{228}Th. For Fe_2O_3 the commercial samples (1) 1360 WF and (2) 1360 Bayferrox were used. (a) Non-isothermal heating in air; heating rate, 5 °C min^{-1}. (b) Subsequent isothermal heating at 1350 °C in $N_2 + 10\% \ O_2$.

iron(III) oxide from Bayer (F.R.G.), which were stated by the producer to posses the same reactivity estimated by the surface area value (2.6 $m^2 \ g^{-1}$).

ETA was recommended [74] for industrial laboratory applications, as the information obtained on reactivity is more accurate with respect to the proper solid-state reaction of ferrite production than surface area measurements by adsorption methods or other traditional techniques.

CONCLUSION

It has been shown in this status report that emanation thermal analysis represents a useful tool for basic research and also for the solution of practical problems of chemical technology, powder metallurgy, plastics production, nuclear science and technology, etc. The easy automation of the method, the availability of commercial apparatus and the recently formulated reliable theory of ETA ensure a bright future for the method.

REFERENCES

1 R.C. Mackenzie, in G. Lombardi (Ed.), For Better Thermal Analysis, Rome, 1979.
2 O. Hahn, J. Chem. Soc. Suppl., S259 (1949).
3 F.W. Felix, J. Phys., 34 (1973) C9-149.
4 S. Ichiba, S. Yajima, S. Kamemoto and K. Shiba, Bull. Chem. Soc. Jpn., 33 (1960) 426; 34 (1961) 133.
5 P. Koss, Acta Phys. Aust., 26 (1976) 250.
6 G. Carter and J.S. Colligon, Ion Bombardment of Solids, Heinemann, London, 1968.
7 D. Chleck, R. Maehl and D. Cuchiarra, Int. J. Appl. Isot., 14 (1963) 581, 593.
8 V. Balek, Thermochim. Acta, 22 (1978) 1.
9 V. Balek and J. Tölgyessy, Emanation Thermal Analysis and Other Radiometric Emanation Methods, Vol. XIIC of Comprehensive Analytical Chemistry (Ed. G. Svehla), Elsevier, Amsterdam, 1984.
10 S. Flügge and K.E. Zimens, Z. Phys. Chem., Abt. B, 42 (1939) 179.
11 K.B. Zaborenko and O.A. Kapustin, Radiokhimiya, 16 (1974) 611, 618.
12 I.N. Beckman, Vestn. Mosk. Univ., No. 3 (1984).
13 G. Carter, Vacuum, 9 (1962) 245.
14 P.A. Redhead, Vacuum, 12 (1962) 203.
15 R. Kelly and Hj. Matzke, J. Nucl. Mater., 17 (1965) 179; 20 (1966) 175.
16 M.D. Norgett and H.B. Lidiard, Philos. Mag., 18 (1968) 1193.
17 J. Kříž and V. Balek, Thermochim. Acta, 71 (1983) 175.
18 J. Kříž and V. Balek, Thermochim. Acta, 78 (1984) 377.
19 V. Balek and J. Kříž, Thermochim. Acta, 81 (1984) 335.
20 W.D. Emmerich and V. Balek, High Temp.-High Pressures, 5 (1973) 67.
21 V. Balek and I.N. Beckman, Chem. Listy, 79 (1984) 19.
22 I.N. Beckman, A.I. Shviryaev and V. Balek, Thermochim. Acta, 104 (1986) 255.
23 E.V. Kornelsen and M.K. Sinha, J. Appl. Phys., 39 (1968) 4546; Appl. Phys. Lett., 9 (1966) 112.
24 Hj. Matzke, in B. Navinšek (Ed.), Physics of Ionized Gases, Institute Jozef Stefan, Ljulbljana, 1970, p. 326.
25 A.Sy. Ong and T.S. Ellemann, J. Nucl. Mater., 42 (1972) 191.
26 H. Schreiner and G. Glawitsch, Z. Metallkd., 25 (1954) 200.
27 P. Meares, J. Am. Chem. Soc., 75 (1954) 3415; Trans. Faraday Soc., 53 (1957) 101.
28 K.B. Zaborenko, D. Nietzold and N.F. Bakeev, Vysokomol. Soedin, Ser. A, 9 (1967) 240.
29 K.B. Zaborenko and I.N. Beckman, Radiokhimiya, 10 (1968) 268, 382.
30 J.N. Gregory and S. Moorbath, Trans. Faraday Soc., 47 (1951) 1064.
31 V. Balek and J. Kroupa, Thermochim. Acta, 22 (1978) 157.
32 F. Strassmann, Z. Phys. Chem., Abt. B, 26 (1934) 362.
33 V. Balek, Farben Lack, 85 (1979) 252.

34 V. Balek, Z. Anorg. Allg. Chem., 380 (1971) 61.
35 G.F. Hüttig, Z. Elektrochem. Angew. Phys. Chem., 47 (1941) 282.
36 J.A. Hedvall, Solid State Chemistry, Elsevier, 1969.
37 P. Gourdier, P. Bussière and B. Imelik, C.R. Acad. Sci., Ser. C, 264 (1967) 1624.
38 C. Quet and P. Bussière, C.R. Acad. Sci., Ser. C, 280 (1976) 859.
39 V. Balek, Sprechsaal, 116 (1983) 978.
40 V. Balek, M. Vobořil and V. Baran, Nucl. Technol., 50 (1980) 53.
41 K.E. Zimens, Z. Phys. Chem., Abt. B, 37 (1937) 231, 241.
42 K.B. Zaborenko and Ju.Z. Mochalova, Radiokhimiya, 10 (1968) 123.
43 R. Thätner and K.B. Zaborenko, Radiokhimiya, 8 (1966) 482.
44 V. Balek and K.B. Zaborenko, Russ. J. Inorg. Chem., 14 (1969) 464.
45 I.N. Odin, V. Balek, B.A. Popovkin and A.V. Novoselova, Vest. Mosk. Univ., Ser. Khim., (1970) 115.
46 V. Balek and J. Götz in J. Götz (Ed.), Proc. 11th Int. Glass Congress, Prague, 1977, Vol. 3, p. 351.
47 S. Bordas, M. Clavaguera-Mora and V. Balek, Thermochim. Acta, 93 (1985) 283.
48 V. Balek, S. Bordas, M. Geli and M. Vobořil, in H.G. Wiedemann (Ed.), Thermal Analysis, Vol. 1, Birkhäuser Verlag, Basle, 1980, p. 403.
49 K.E. Zimens and H.D. Freyer, Bibliography for Nuclear Research, AED-C-21-01 (1966), AED-C-21-02 (1968).
50 K.E. Zimens and W. Miekeley, Bibliography for Nuclear Research, AED-C-21-03 (1973).
51 K.B. Zaborenko, V.P. Polyakov and J.G. Shoroshev, Radiokhimiya, 7 (1965) 324, 329.
52 M.E. Levina, B.S. Shershev and K.B. Zaborenko, Radiokhimiya, 7 (1965) 480.
53 A.I. Czeckhovskikh, D. Nietzold, K.B. Zaborenko and S.I. Volfkovich, Zh. Neorg. Khim., 11 (1966) 1948.
54 C. Quet, P. Bussière and R. Fretty, C.R. Acad. Sci., Ser. C, 275 (1972) 1077.
55 D.J. Chleck and D. Cucchiara, Int. J. Appl. Radiat. Isotop., 14 (1963) 599.
56 Hj. Matzke, Int. J. Appl. Radiat. Isotop., 27 (1976) 27.
57 G.M. Zhabrova, S.Z. Roginskij and M.D. Shibanova, Kin. Kataliz, 6 (1965) 1018.
58 Č. Jech, Proc. 2nd Int. Congress on Catalysis, Editions Techniques, Paris, 1961, p. 2285.
59 I.N. Beckman and V.V. Teplyakov, Vestn. Mosk. Univ., 1974.
60 V. Balek, Thermochim. Acta, 72 (1984) 147.
61 V. Balek and J. Dohnálek, J. Mater. Sci., 17 (1982) 2281.
62 V. Balek, J. Dohnálek and W.D. Emmerich, in H.G. Wiedemann (Ed.), Thermal Analysis, Birkhäuser Verlag, Vol. II, p. 375.
63 D.J. Chleck, IAEA Symposium on Radioisotope Traces in Industry and Geophysics, Prague, 1966, Pap. SM-84/4 (1966).
64 V. Jesenák, J. Tölgyessy, Š. Varga and B. Sílaš, Silikáty, 15 (1971) 65.
65 V. Jesenák, J. Tölgyessy, Š. Varga and B. Silaš, Jad. Energ., 16 (1971) 375.
66 V. Balek, and J. Dohnálek, Silikáty, 26 (1982) 231.
67 V. Balek, O. Kříž, J. Fusek and D. Jiroušová, Rep. Nucl. Res. Inst. Řež, No. 7655 (1985).
68 V. Balek, J. Am. Ceram. Soc., 53 (1970) 540.
69 G.F. Hüttig, H. Wörl and H.H. Weitzer, Z. Anorg. Chem., 283 (1956) 207.
70 S. Ichiba, J. Nucl. Sci. Technol., 2 (1965) 163.
71 G. Wolf, L. Ochs and F. Strassmann, in Radioisotopes in Scientific Research, UNESCO Conf., Paris, 1957, Vol. 1., Pergamon Press, London, 1958, p. 516.
72 K.B. Zaborenko, R. Thätner and L.L. Melikhov, Radiokhimiya, 5 (1963) 360.
73 K.B. Zaborenko, A.M. Babeshkin and L.L. Melikhov, Izv. Vuzov., Ser. Khim. Khim. Tekhnol., 3 (1960) 288.
74 V. Balek, J. Appl. Chem. (London), 20 (1970) 73.
75 V. Balek, J. Therm. Anal., 12 (1977) 111.
76 V. Balek, J. Therm. Anal., 20 (1981) 495.

POSSIBILITIES OF EMANATION THERMAL ANALYSIS IN THE STUDY OF STRUCTURAL ALTERATIONS IN COAL

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A variety of experimental techniques have been used to study the pore development of British coals (Manvers and Markham) during pyrolysis.

The total porosity was found to increase with temperature up to a maximum at approximately 800 °C; similarly, micro- and mesoporosities increased at temperatures up to 800 °C before decreasing.

The initial mechanism was found to be the unblocking of closed pores and pore generation by removal of material. Large pores increase by pore enlargement and pore combination. Further changes that occur are due to structural rearrangements only [1,2].

We have also used emanation thermal analysis for the study of structural alterations [3]. It was shown [4] that emanation thermal analysis reflects quantitatively the development of the microstructure of coals and can therefore be used as a "fingerprint" technique for following these changes with heat treatment directly. Information obtained by ETA enabled us to discern other processes such as release of volatiles from coal and char samples.

Owing to its versatility, ETA can be recommended as a supplementary technique for characterizing coal and char samples during pyrolysis.

REFERENCES

1 J.L. Johnson, Kinetics of Coal Gasification, Wiley, New York, 1979.
2 A. De Korányi and S.G. Williams, Thermochim. Acta, 82 (1984) 103.
3 V. Balek, Thermochim. Acta, 22 (1978) 1.
4 V. Balek and A. De Korányi, Proc. 8th ICTA '85, Bratislava, Thermochim. Acta, 93 (1985) 737.