

THERMAL ANALYSIS OF SOME FLY ASHES

II. Self-hardening activity of fly ashes

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Abstract

The self-hardening activity of fly ashes was investigated looking for the possibility of their chemical reactions with water without additives. A method had to be developed for separation of the structural water from the adsorbed or free one. The decomposition of the chemically bound water was measured by thermogravimetry. The 'P' dimensionless number proved to be applicable for the quantitative characterisation of the measured data with more DTG peaks. The examined reaction depends on the chemical composition and the physical structure of the fly ashes and the time of interaction with water. The SO₃ content seems important, but the characteristics of the formed compounds differ deeply from the CaSO₄·2H₂O. The observed and examined reaction is an important factor of the self-hardening process of fly ash deposits.

Keywords: deposit, dimensionless evaluation, fly ash, reaction with water, self-hardening

Introduction

Coal is one of the most important raw material of power stations, but they produce large volume of slag and ashes as waste. Several hundred kilograms per head is the average production of fly ash in different countries yearly [1]. The cost of deposition of this solid waste is great and increasing very quickly by the expanding requirements of environmental protection, e.g. the cost of deposition was about 200 USD/t in Germany and has multiplied during 15 years 24–26 times in the USA [2]. A program began to develop about fifty years ago for decreasing the costs and problems of deposition looking for the application possibilities of fly ashes as secondary raw materials. The domains of industrial fly ash applications are very wide today [e.g. 2, 3].

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The chemical composition and other properties of fly ashes depend not only on the type of coal but on the burning conditions as well [4]. Very important is the composition and structure of the fly ashes in case of their deposition, because the leaching of the toxic components (heavy metals, dioxins, radioactive materials, etc.) can contaminate the water sources. The leaching capacity influences first of all the need and costs of the isolation of the deposits.

The most valuable industrial application of fly ashes is based upon their latent hydraulic, so-called pozzolanic property that can be activated by basic additives like lime or portland cement. This phenomenon was known from the Roman times, and there are well developed and standardised systems for measuring the pozzolanic activity [e.g. 5–7].

It is a known fact, however, that the fly ash deposits can harden within limited time and without additives with basic properties, too. The reason of this self-hardening of fly ashes was not examined till now, though this process probably influences the leaching properties. Consequently, this phenomenon has increasing importance from the aspect of environmental protection, if deposition is the single possibility for the elimination of fly ash as waste material. Thermogravimetry (TG) and differential thermogravimetry (DTG) together with the 'I' dimensionless evaluation [8] of the measured data proved a good or perhaps the sole method for this examination nowadays.

Experimental

The samples for the investigation of the self-hardening effect were collected from the electrical precipitators of boilers fired with powdered coals. Samples 1 and 2 were fly ashes of bituminous coals, while samples 3 and 4 of lignite.

The mass ratio of the mixed fly ash samples and distilled water were 2:1 and the mixtures were kept under saturated water vapour at 25°C. A method was applied to remove the not reacted free water before the TG measurements. These measurements have been carried out in air atmosphere with a thermobalance type Derivatograph-C (MOM, Budapest). The heating rate was 10 deg·min⁻¹ and the sample mass was 150–650 mg depending on the probable weight change (chemically bound water content). The measurements were repeated with the mixtures of water and ashes after 1, 7 and 28 days respectively.

The results of oxide analysis of the ashes are given in Table 1.

The composition of the original samples was determined by X-ray diffraction [9] and the thermal properties by simultaneous TG, DTG and DTA measurements [9].

The X-ray analysis of the original samples showed, that all of them contain CaSO₄, α-SiO₂ and α-Fe₂O₃. Besides these components sample 3 contains FeS and sample 4 contains Al₂SiO₅.

CaCO₃ and hydrated CaO were found, too, in the original fly ash samples 1 and 2 with TG measurements [9]. In all the samples a certain amount of un-

Table 1 Chemical composition of the fly ashes/weight %

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃
1	15.7	10.6	4.5	48.0	3.7	0.1	0.3	15.5
2	48.0	16.8	5.0	17.3	1.8	0.7	1.3	7.4
3	46.2	20.5	11.6	10.3	1.6	0.2	0.9	8.0
4	61.0	17.7	7.5	5.9	1.7	0.3	0.9	4.3

burned carbon was found beside these components. The carbon content of the samples 1 and 2 was very small (~0.1%), but in the samples 3 and 4 the carbon content amounted up to 4%.

Because the free water quantity is much more in the original mixtures of water and fly ashes, it is obvious by TG measurements that the evaporation of the free water content of the mixture can overlap the decomposition of the chemically bound one. Consequently, it was necessary to develop a method for the separation of the adsorptive or free water from the chemically bound one. The samples were treated for this purpose with ethyl alcohol or acetone for 30 min and dried using vacuum filter for another 30 min after the definite reaction times (1, 7, 28 days). The premeasurements showed that both the ethyl alcohol and the acetone remove the adsorptive and free water and they have no effect on the chemically bound water. The samples were dried for the TG measurements in most of the cases with acetone because of its greater vapour pressure.

Results of TG measurements

The Figs 1–4 show the measured TG and DTG data of the 1, 7 and 28 days old mixtures of water and fly ashes dried with acetone. It can be seen that the chemical reactions of the water with fly ashes depend on the time and the temperatures of the maximum of the DTG peaks shift to higher temperature.

The TG and DTG curves of the samples 1 and 2 seem completely different from the corresponding curves of samples 3 and 4.

There is a relatively high CaO content in samples 1 and 2 (Table 1). CaO in contact with water reacts intensively forming Ca(OH)₂. On the other hand, it follows from the SO₃ contents of the samples that the alkali and alkaline-earth metals can be present as sulphates and some of them form hydrates easily. For example the FeSO₄·7H₂O and the CaSO₄·2H₂O loses their crystal water up to about 200°C [e.g. 10–12] and this mass loss can correspond with the measured TG and DTG data.

In sample 1 there is a slight mass loss among 180 and 400°C that changes a little during the hydration time from 1 to 28 days. In this temperature range the hydration process could correspond to the dehydration of calcium aluminates [13].

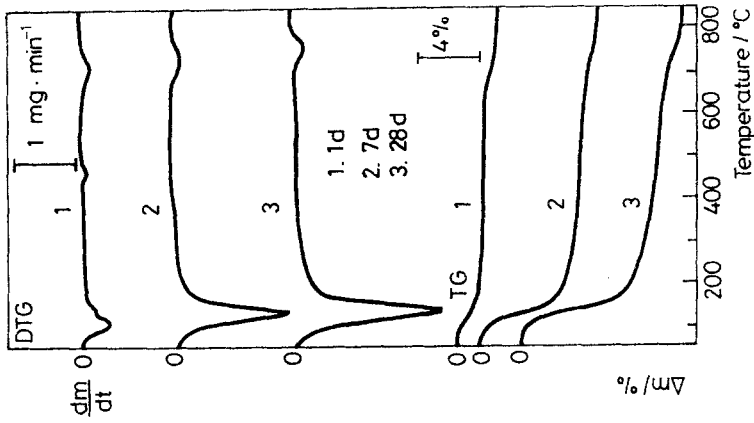


Fig. 2 TG and DTG curves of reacted sample 2

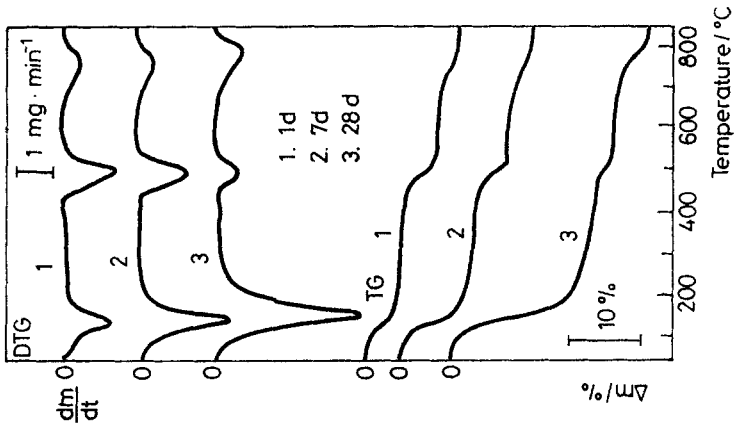


Fig. 1 TG and DTG curves of reacted sample 1

The observable weight decrease of sample 1 is in strict connection with the decomposition of the $\text{Ca}(\text{OH})_2$ in the temperature range from 400 to 500°C [9, 14]. The mass loss of the sample 2 was less (up to 2.5%) in the temperature range from 180 to 600°C and one part of it is probably due to the water loss of $\text{Ca}(\text{OH})_2$ (see the 1 day TG and DTG curves on Fig. 2). The mass loss process of sample 1 corresponds to the decomposition of CaCO_3 at about 750°C [e.g. 15].

The TG curves of the sample 1 show that the $\text{Ca}(\text{OH})_2$ content decreases with time, correspondingly the amount of CaCO_3 increases because to the CO_2 content of the air react with the $\text{Ca}(\text{OH})_2$. It can be supposed that this process also contributes to the self-hardening of fly ashes.

The self-hardening effect of sample 1 was observable the first day of its mixing with water and at 28 days the sample was hard. The effect of water on sample 2 was not so explicit.

The chemical compositions of the samples 3 and 4 are completely different from that of the samples 1 and 2 (Table 1). The fly ashes of these samples originated from lignite. The CaO contents of these samples are low, while the amount of SiO_2 and Al_2O_3 are high. The reaction of samples 3 and 4 with water seems also different. This difference can be observed very well on the TG and DTG curves of Figs 3 and 4.

The decomposition of the chemically bound water of the examined samples starts at room temperature and is independent of the interaction between water and fly ashes.

The hydrated CaO and the CaCO_3 content of the samples can be calculated easily from the weight change data of the TG curves, but it is possible to get more information on the water quantity that reacted with the fly ash and measured among 40 to 280°C decomposition temperature. Table 2 contains these data beside the hypothetical $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and its water content calculated from the SO_3 (CaO) content of the fly ash samples.

It can be concluded from the quantity and the decomposition temperature interval of hydrate waters that there is not any direct connection between the hydration of the fly ash samples and their hypothetical gypsum content.

This is proved by the results of the functions of the connecting kinetic compensation effects (CE). The CE as linear function between the logarithm of the

Table 2 The chemically bound water content of the 28 day's mixtures and the hypothetical $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Sample mark	Gypsum	1	2	3	4
$T_{\text{interval of dec.}}/^\circ\text{C}$	120–182	70–220	50–200	50–190	50–180
Hydrated water/%	21.80	20.13	7.56	3.32	5.08
Hypothetical water of gypsum/%	20.93	6.98	1.87	3.60	1.94

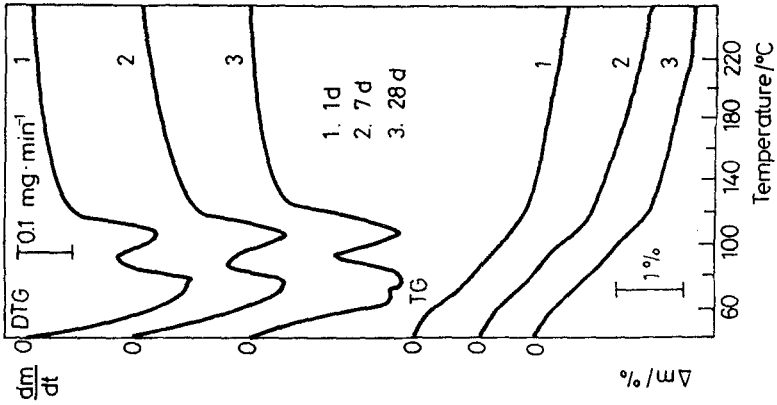


Fig. 3 TG and DTG curves of reacted sample 3

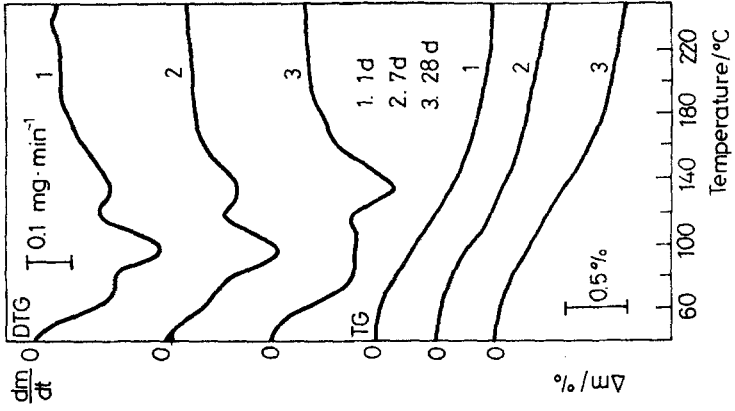


Fig. 4 TG and DTG curves of reacted sample 4

pre-exponential factor ($\ln A$) and the activation energy (E) calculated from the formal kinetic evaluation of the measured TG and DTG data. The $\text{tg}\alpha$ of the CE characterises the decomposition process [e.g. 16–18]. According to this and giving the ' r ' value, too, the $\text{tg}\alpha$ of the CE of

the hydrated sample 1 is $7^{\circ}53'48''$ (with plenty of CaO content), ($r=1.0000$)

the hydrated samples without sample 1 is $8^{\circ}20'51''$, ($r=0.9999$)

all the hydrated samples is $8^{\circ}17'31''$ ($r=0.9996$).

From the TG, DTG measurement of gypsum the $\text{tg}\alpha$ of the CE of

the first DTG peak is $16^{\circ}41'58''$, ($R=1.0000$)

the second DTG peak is $15^{\circ}47'22''$, ($r=1.0000$)

all data pairs is $16^{\circ}32'28''$ ($r=0.9995$).

Dimensionless evaluation of TG measurements

It is known that the shape of TG and DTG curves depend on the measuring conditions, consequently the comparability of the measurements is very limited and it is confined to the qualitative comparison in most of the cases. Limited is the applicability of the formal kinetic analysis of the measured TG data, too, because the calculated kinetic constants depend also on the measuring conditions and on the method of calculation strongly. The basic reasons of these phenomena are the complexity of the decomposition processes. The elimination of the complexity is impossible at present. So, instead of looking for some kinetic constants, investigations of the dependence of the decomposition processes from the factors (measuring conditions, different materials) can lead to the expression of the analogy of TG measurements. The dimensionless analysis of the TG data [8] proved to be applicable for this purpose, too, in the case of the examination of the self-hardening process.

The base of the applied 'I' dimensionless number is the very extensively used and known differential Eq. (1).

$$-d\alpha/dt = A \exp(-E/RT)(1-\alpha)^n \quad (1)$$

where:

$-d\alpha/dt$ velocity of decomposition (from the measured (DTG)_i)

$(1-\alpha)$ fraction not reacted (from the measured (TG)_i)

A pre-exponential factor

E activation energy

R universal gas constant

T temperature (from the measured °C_i)

n order of reaction.

The 'I' dimensionless number can be calculated with the following Eq. (2), saving the usual structure and marks of Eq. (1) but only formally:

$$I_i = E_i/RT_i = \ln A + n \ln(1-\alpha)_i - \ln(-d\alpha/dt)_i \quad (2)$$

The Eq. (2) is suitable for the requirement, namely to determine how I_i depends on the measuring conditions and on the system of the superposed partial processes of the decomposition. The I_i is a direct function of the measured TG_i , DTG_i and T_i data if for the basic calculations $A=1$ and $n=1$ are introduced.

The result is E_i by multiplication of I_i with RT_i and it is possible to express the degree of analogy of different measurements by the following functions:

$$I_i \text{ vs. } (1-\alpha)_i \quad (3)$$

$$I_i \text{ vs. } 1/T_i \quad (4)$$

$$E_i \text{ vs. } (1-\alpha)_i \quad (5)$$

$$E_i \text{ vs. } 1/T_i \quad (6)$$

The application of Eq. (4) is enough to show the quantitative connections among the different measurements looking for the self-hardening effect. From this aspect the first task is to look for the type of the formed compounds and the second task is to look for the effect of the reaction time and the properties of the fly ashes.

There are $CaSO_4 \cdot 2H_2O$, FeS , $\alpha-SiO_2$, $\alpha-Fe_2O_3$, Al_2SiO_5 beside CaO and SO_3 in the samples 1–4 according to the X-ray analysis of the original fly ashes [9]. Consequently, it was advisable to measure beside the water and fly ash mixture some other thermal processes as follows:

- i. the thermal dehydration of $CaSO_4 \cdot 2H_2O$
- ii. the hydration product of tricalcium aluminate (C_3A) as one clinker mineral
- iii. the hydration product of tricalcium aluminate after mixing with gypsum (CS) and the drying process of different powders, namely
- iv. the SiO_2 (25–50 μm),
- v. the Al_2O_3 (25–70 μm),
- vi. the Air Cleaner Fine Test Dust measured with ANL 8 N US (ACFTD).

Plotting of all the measured I_i vs. $1/T_i$ functions would decrease the lucidity of the curves, so Fig. 5 shows only the I_i vs. $1/T_i$ functions of the 28 days old sample 1, the gypsum and the drying process of SiO_2 (25–50 μm) – water mixture. These results were chosen for showing the character of the examined functions and for helping to conclude from the data of Table 3, where all the important and connecting results for comparison and discussion the TG measurements are shown.

Table 3 shows the $1/T_i$ and the I_i values connecting to the similar $(1-\alpha)_i$ intervals, namely the beginning and ends of the measurement. Among others the great $1/T_i$ interval differences are obvious.

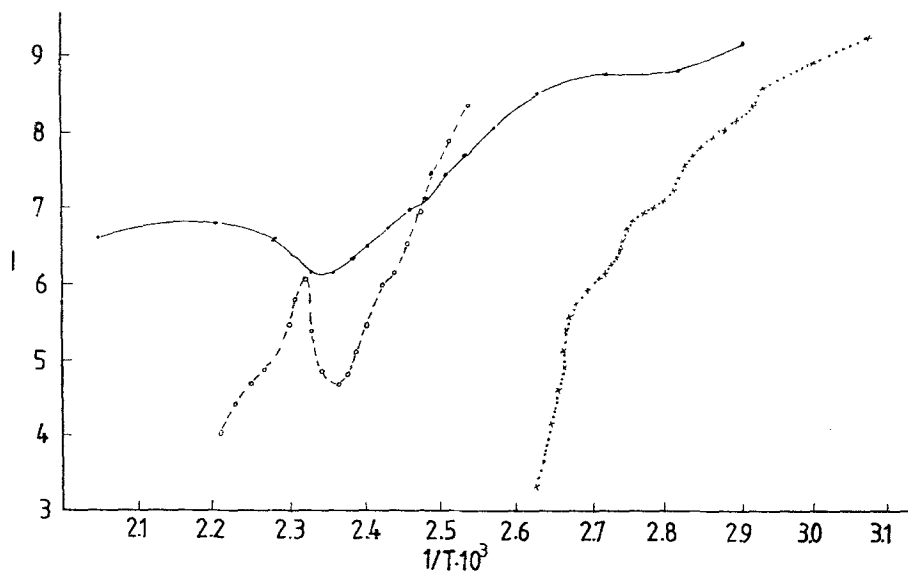


Fig. 5 I_i vs. $1/T_i$ functions of the 28 days old sample 1, the gypsum and the SiO_2 (25–50 μm) (— sample 1; 28 days, ○— — gypsum, ×····· SiO_2)

Table 3 Comparison of the I_i vs. $1/T_i$ functions

Sample	Time of treatment/ day	Interval of		
		$(1-\alpha)_i$	$(1/T_i \cdot 10^3)$	I_i
1	1	0.990–0.111	3.057–2.374	9.561–5.870
	28	0.959–0.037	2.908–2.040	9.168–6.598
2	1	0.903–0.030	2.840–2.456	7.667–3.397
	28	0.976–0.030	3.133–2.137	9.281–6.320
3	1	0.939–0.015	3.085–2.596	6.997–3.356
	28	0.942–0.035	3.056–2.162	7.898–5.181
4	1	0.951–0.062	3.084–2.590	6.511–5.112
Gypsum		0.966–0.065	2.537–2.212	8.354–4.006
C_3AH^*	28	0.968–0.028	2.680–1.230	8.335–4.556
$\text{C}_3\text{ACSH}^{**}$	28	0.960–0.029	2.644–1.364	7.925–6.320
SiO_2		0.992–0.053	3.075–2.631	9.256–3.303
Al_2O_3		0.979–0.021	3.114–2.666	9.053–2.424
ACFTD		0.974–0.078	3.043–2.583	8.934–3.941

* C_3AH = Tricalcium aluminate hydrate

** C_3ACSH = Hydrate of tricalcium aluminate and gypsum mixture after 28 days

The conclusion is that the thermal decomposition of the formed compounds by the reaction of water and fly ashes differs characteristically from the examined other thermal dehydrations, namely from that of the gypsum, from that of one supposable clinker minerals (C_3AH) and its practically very important reaction with gypsum (C_3ACSH) and from that of mixtures of water with different fine powders controlling with these the method of drying with acetone as well.

The effects of time in the self-hardening process are demonstrated by Fig. 6, comparing the I_i vs. $1/T_i$ results of the 1 and 28 days old hydrated sample 1.

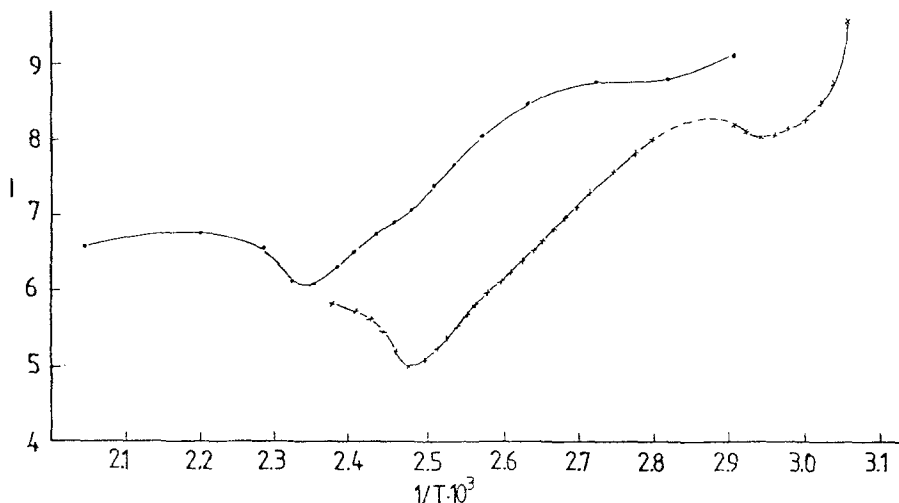


Fig. 6 I_i vs. $1/T_i$ functions of the 1 and 28 days old hydrated fly ash (sample 1; \times 1 day; \cdot 28 days)

Conspicuous is the similarity of the shape of the two curves. It is easy to conclude that the reaction is relatively quick among the water and the fly ash. Remembering to the hardening of portland cement as analogy, it can be supposed that the formed compounds has colloid character because only the bond energy of hydrate water is increasing as the effect of the reaction time. The function of the 1 day old sample is transformable quantitatively to the 28 days old one by increasing the dehydration temperature with $-0.133 \cdot 1/T_i \cdot 10^3$ and $0.935 I_i$.

The Figs 7 and 8 show the results about the chemical and physical properties of different types of fly ashes. The I_i vs. $1/T_i$ functions of the 1 day old samples 1 and 4 can be seen in Fig. 7 and the 28 days old results of the samples 1, 2 and 3 are shown in Fig. 8. The base characters of the functions are similar, but the details depend on the chemical and physical properties of the fly ashes.

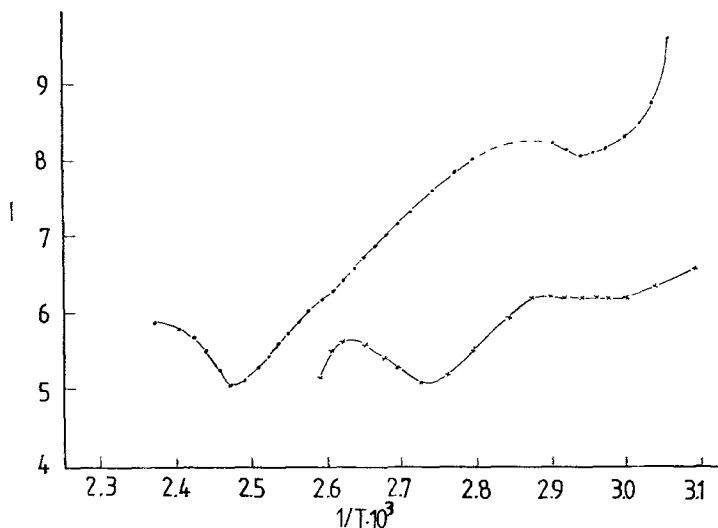


Fig. 7 I_i vs. $1/T_i$ functions of the 1 day old hydrated fly ashes (\cdot sample 1, and \times sample 4)

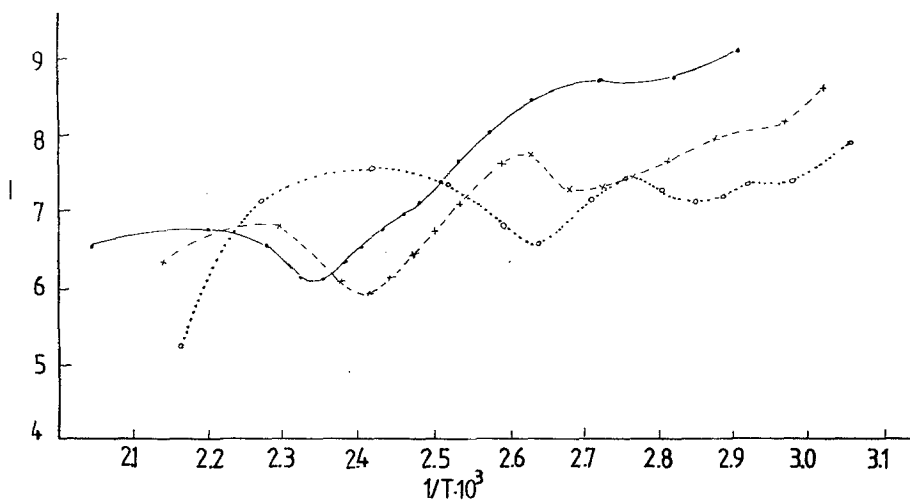


Fig. 8 I_i vs. $1/T_i$ functions the 28 days old hydrated fly ashes (\cdot — sample 1, \times - - - sample 2, \circ sample 3)

Conclusions

The self-hardening process of the fly ashes is a hydration process. The TG measurements connected to the dimensionless evaluation of the data are suitable for the research of the process and the formed compounds.

The I_i vs. $1/T_i$ function is very well suitable for the characterisation of the formed compounds of the self-hardening process but the details of the shape of

the functions depend on the chemical and physical properties of the examined fly ash.

The colloid character of the formed compounds can be supposed.

The carbonisation of the CaO content and the hydration of the CaSO₄ content of the fly ashes can take some part in the self-hardening process, too.

The dimensionless evaluation is suitable for the quantitative comparison of the TG data with more DTG peaks as well.

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