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THE HYDRATION OF CEMENT INVESTIGATED BY EMANATION THERMAL ANALYSIS

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ABSTRACT

The application of the emanation thermal analysis in the investigation of cement and clinker minerals hydration is shown. The method enabled us to follow continuously changes in the microstructure of the hydrating paste at the required temperature and humidity as well as in the presence of various admixtures. The comparison of the ETA results with those obtained by commonly used methods showed that ETA gives the possibility of new insights into the evolution of the cement paste structure and represents a powerfull tool in the study of the initial stage of the hydration of cement and clinker minerals.

INTRODUCTION

In spite of the vast amount of literature discussion about the hydration of cement /ref. 1/ there is a gap remaining in our knowledge concerning the cement-water interaction occuring during the first few hours of hydration. The effort concentrates on the study of the hydration of tricalciumsilicate /C_3S/, the most important component of portland cements, responsible for most of the engineering properties of hardened cement paste, such as strength, dimensional stability, etc. As soon as a precise control of the development of microstructure will be achieved, it will lead to the improvement of the technology of the production of concrete elements and, ultimately to the greater realization of the potential of portland cement.

Numerous attempts have been made to explain the complex processes of the C_3S and cement hydration. Calorimetry, analysis of the liquid phase composition, surface area and porosity measurements, as well as electron microscopy have been the most commonly used experimental approaches. Furthermore, other properties have been used to evaluate the setting and hardening of the cement paste - such as penetration resistance, strength development, determination of non-evaporable water content, etc. In recent years these have been supplemented by thermoluminiscence, silicate polymerization analysis and other techniques, e.g. the emanation thermal analysis.

The aim of this paper is to show the potentialities of the emanation thermal analysis /ref. 2/ in the investigation of the hydration of cement and clinker minerals. This method enabled us to receive a new insight into the initial stage of cement hydration.

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PRINCIPLES OF THE EMANATION THERMAL ANALYSIS

Definition of the method

The emanation thermal analysis /ETA/ is based on the measurement of radioactive inert gases, historically called the emanation, released from the material studied. The temperature and other parameters of the sample and surrounding medium are controlled during the determination of the inert gas released. Inert gases do not react with the solid, in which they are incorporated in trace amounts before the measurement. The amount of inert gas released depends on the physico-chemical processes taking place in the solid or on the surface of the solid studied.

Labelling of samples

The sample can be labelled using, for example, the parent isotopes of radon, such as Th-228 or Ra-224. The atoms of Rn-220 are formed by spontaneous decay as shown by Eq. 1:

$$^{228}\text{Th} \xrightarrow{\alpha} {}^{224}\text{Ra} \xrightarrow{\alpha} {}^{220}\text{Rn} \qquad /1/$$

The cement sample can be labelled by impregnation with a non-aqueous /acetone/ solution containing Th-228 and Ra-224 in the concentration of the order of 10^5 s^{-1} cm^{-3}. The radionuclides are adsorbed on the surfaces of the cemen grains and the non-aqueous solvent is evaporated. The specific activity of the samples labelled is 10^3 - 10^4 s^{-1} g^{-1} of sample. The atoms of Ra-224 and Rn-220 are incorporated into the cement grains to a maximum depth of 120 nm as a consequence of the recoil energy 85 keV/atom which every atom gains during the decay of its parent /ref. 2/. The concentration of Ra-atoms and Rn-atoms in the labelled cement grains decreases practically linearly from the surface towards the grain center.

The processes of radon release from solids

The release mechanisms of Rn-atoms from a grain of solid are schematically shown in Fig. 1. When no structure changes or chemical transformations take place in the solid studied, the release of radon is controlled by the diffusion of radon within the solid material and by the recoil energy which every Rn-atom gains during its formation from the atoms of radium.

The rate of the release of radon atoms from the solid depends on the structure changes or chemical processes which may take place in the solid or on it surface. An interaction of the labelled sample with the surrounding medium or a change occuring within the solid sample causes a sudden release of atoms fixed in the structure of the sample.

The relative rate of radon release from the sample in the steady state depends on the surface area and the coefficient of radon diffusion in the solid. The emanating power E, defined as the rate of radon release A_{rel} related to the rate of radon formation A_{form} by the decay of radium, of an isolated grair of the sample of the size d $\geq$ 1 μm can be expressed in a simplified way by Equation 2:

$$E = S_{eff}\left[K_1 + K_2(D/\lambda)^{1/2}\right]\cdot\rho \qquad /2/$$

where S_{eff} is the effective surface area related to the mass of the sample, K_1 K_2 are constants, D is the coefficient of Rn diffusion in the solid, ρ is the density and λ is the decay constant of the Rn-atoms.

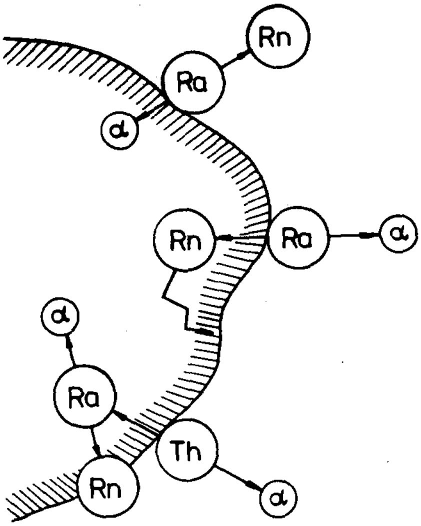

Fig. 1. Mechanisms of radon release from a grain of solid labelled by the surface impregnation with Th-228 and Ra-224 nuclides.

EXPERIMENTAL

Sample preparation

Tricalcium silicate /C_3S/ samples studied were prepared by high temperature synthesis in the Institute of Inorganic Chemistry, Berlin /GDR/ and by grinding to a different degree. The surface areas of the samples are: $S = 0.3\ m^2/g$ - sample A; $1.2\ m^2/g$ - sample B; and $0.4\ m^2/g$ - sample C, resp. The C_3S powder was labelled by the impregnation technique with Th-228 and Ra-224 nuclides /ref. 2/. The thermal activation of C_3S was performed by heating to 600 °C in air followed by rapid cooling.

The portland cement, designated PC-400, was from Lochkov, Czechoslovakia. The samples were labelled by the same impregnation technique as C_3S.

The samples of the water suspensions of C_3S or cement were prepared by the addition of water to solid labelled samples in the ratio water/solid = 0.4 /for C_3S/ and 0.3 /for cement/, resp.

ETA measuring procedures

The samples of the suspensions in an amount of about 3 g were homogenized by mixing and put in a PVC vessel into the measuring device. The apparatus for the ETA is schematically shown in Fig. 2.

The sample is held in the measuring cell at the required temperature and air is streamed through at a constant flow-rate, so that the radon atoms released are transported into the detection chamber. The carrier gas, its humidity and chemical composition, can be chosen according to the requirements of the experiment. Before placing the sample into the measuring cell, the experimental conditions were adjusted: the temperature ranged from 20 to 85 °C, the carrier gas was air saturated with water vapour to a relative humidity of 95 ±3 %. The high relative humidity protected the sample from drying outduring the experiment. The temperature of the sample was kept constant by means of

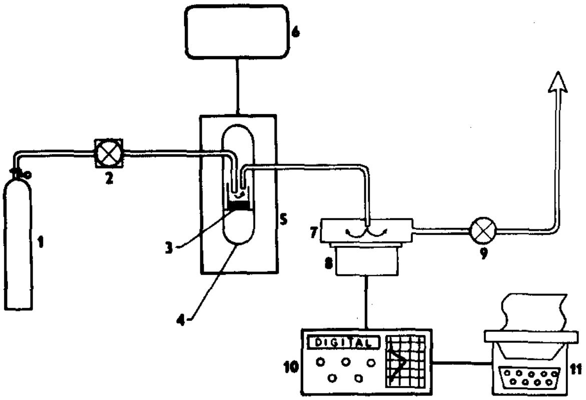

Fig. 2. Scheme of the apparatus for the emanation thermal analysis. 1- carrier gas supply; 2- stabilizer and flowrate meter of the carrier gas; 3- the sample measured; 4- the measuring cell; 5- the thermostat; 6- the temperature controller of the measured sample; 7- the detection chamber of the radon radioactivity; 8- the alpha-radioactivity detector with a photomultiplier; 9- the flow-rate of the carrier gas; 10- the impulse counter; 11- the printer.

a thermostat; for the detection of the alpha radiation of radon a scintillation detector with a photomultiplier was used in connection with an impulse counter provided by an output to the printer. The commercially available ETA apparatus produced by NETZSCH Ltd., Selb /F.R.G./ represents a part of a series of instruments for simultaneous thermal analysis /ref. 4/.

The ETA results are presented as time dependences of the relative radon release rate E, calculated from experimental data as $E = A_{gas}/A_{solid}$, where A_{gas} is the radioactivity of radon released from the sample measured in the dynamic conditions of the experiment, and A_{solid} is the total radioactivity of the sample, being proportional to the rate of radon formation in the sample.

Measuring processes using other methods /ref. 5/

Penetration resistance, R_F, was determined as a ratio of the strength needed for the penetration of a cylindrical indentor of an area of 1 mm^2 into a sample of the setting cement paste to a depth of 5 mm to the cross-sectional area of this indentor /ref. 6/.

The time dependence of the hydration reaction was investigated by means of conductivity calorimetry /ref. 7/. The standard Vicat test was used for checking the beginning and the end of the setting period of cement paste.

RESULTS AND DISCUSSION

Hydration of tricalciumsilicate /C_3S/

Fig. 3 shows the time dependence of the release rate of radon from C_3S-water suspension, measured by ETA isothermally at 25 °C. After mixing C_3S with water the hydration reactions take place starting from the surface of the grains. The interactions of water with C_3S surface create new pathes for radon release from the grain, which result in a sudden increase of the release rate of radon from the suspension.

We can suppose /ref. 8/ that at the very beginning of the hydration reactions the radon release rate is directly proportional to the velocity of the interaction between C_3S grains and water. This supposition is generally valid

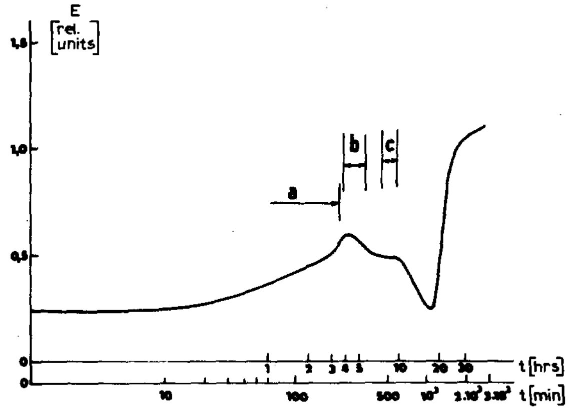

Fig. 3. The time dependence of the radon release rate /ETA curve/ measured during the hydration of C3S at 25 °C.
Following time intervals are indicated by letters:
/a/ the interval in which the hydration in the radioactive labelled surface layer takes place;
/b/ the interval in which the surface area of the hydrated products attains the maximum value;
/c/ the interval in which the surface area of the total hydrated sample attains the maximum value.

when the distribution of the Rn-atoms in the surface layers is uniform and when hydration products formed cause no obstacles for the movement of the Rn-atoms from the reaction place to the sample surface.

However, in the further stage of the hydration process the structure of the hydration products can slow down the rate of the radon release. It must be taken into account that the hydration products contain atoms of Th-228 and Ra-224 which are incorporated from the labelled grains of C_3S. Consequently the radon atoms released from the hydrated products, together with those released during the decomposition of the anhydrous phases, contribute to the rado release rate of the sample measured.

The time in which the reaction of the C_3S grains with water will proceed in the depth of approx. 120 nm from the surface is estimated to be not greater than 200 minutes, depending on the grain size /see the time interval a in Fig.3/. After this time, the radon atoms released from the paste have their origin only in the hydrated products, and the radon release rate will reflect the permeability of their structure for radon atoms. As the structure of the hydration products is not stable, but is expected to undergo changes, the measured radon release rate indicates the changes and the development of the paste structure.

As it has been shown by the surface area measurements /ref. 9/, the surface area of the hydrated products increases from the beginning of the hydration, in the time between 4 and 6 hours of the reaction it reaches its maximum value, S = 78 - 80 $m^2 g^{-1}$ /cf. interval designated b in Fig. 3/. The maximum surface area, S = 11 $m^2 g^{-1}$ of the whole sample is attained in the time between 8 and 10 hours from the beginning of the hydration /cf. the interval c in Fig.3/.

We can therefore state that in the first 200 minutes after the mixing C_3S with water the hydration process takes place in the radioactive labelled layer, estimated as 120 nm thick. From the results of ETA we can obtain the quantitative characteristics of the rate of the C_3S hydration at the very beginning of the reaction.

In the subsequent time interval the ETA reflects the development of the microstructure of hydrated products which control the evolution of the mechanical properties of the paste. In the next, the results of the ETA investigations of

C_3S hydration will be shown as influenced by various effects.

Effect of the surface area. In Fig. 4 we compare the ETA curve of the C_3S water suspension of C_3S samples differing in their surface area /0.3 and 1.2 $m^2 g^{-1}$, resp./. As it has been mentioned earlier, at the very beginning of the hydration reaction, the radon release rate indicates the velocity of the interaction between C_3S and water. The slope of the time dependence of the radon release in the time interval up to approx. 200 min can be used as the parameter for characterizing the C_3S-water interaction in its initial stage.

In the progress of hydration, the radioactive labelled C_3S layer gradually changes into the hydrated products C-S-H. The effects on the ETA curve indicate the changes of the microstructure of the hydrated products, namely in the range of micropores, the size of which is comparable with the diameter of the radon atom /d = 0.4 nm/.

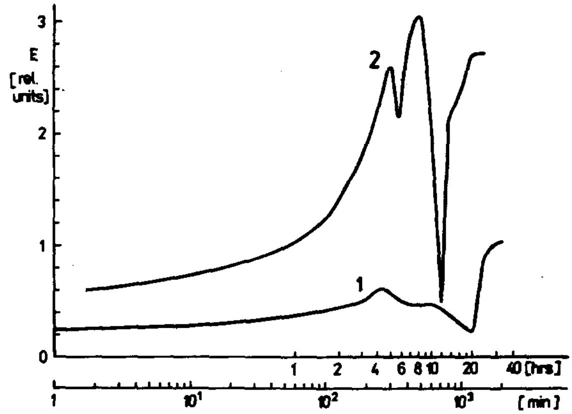

Fig. 4. ETA curves of C_3S hydration at the temperature of 25 °C /the C_3S was mixed with water in the ratio water/solid = 0.4/. The C_3S samples differ in the surface area values: Sample A - S = 0.3 $m^2 g^{-1}$ /curve 1/; Sample B - S = 1.2 $m^2 g^{-1}$ /curve 2/.

Therefore we propose the parameter $\Delta E = E_{100} - E_{10}$, corresponding to the radon release rate change in the interval from 10 to 100 minutes after the mixing C_3S with water, to assess the velocity of the C_3S-water interaction. By means of this parameter the difference in the hydration of C_3S samples of different surface areas have been evaluated /see Fig. 4/. For the sample A /surface area S = 0.3 $m^2 g^{-1}$/ we obtained the parameter $\Delta E = 0.154$, for the sample B /surface area S = 1.2 $m^2 g^{-1}$/, $\Delta E = 0.485$. The sample of C_3S of a 4 times higher surface area is characterized by approx. 3 times higher velocity of the interaction with water. The general character of the ETA curves during the hydration at 25 °C is similar, the effects in the curve 1, corresponding to the larger surface area are more pronounced.

Effect of thermal activation. Fig. 5 shows the ETA curves of C_3S hydration of thermally activated /curve 1/ and non-activated /curve 2/ C_3S samples The surface area values /S = 0.4 $m^2 g^{-1}$/ of both of the samples C_1 and C_2 are identical. On the base of the ETA curves in Fig. 5 we are able to distinguish the differences between the reactivities of the thermally activated and non-activated samples. The activated sample is characterized by the value of $\Delta E = 0.773$ whereas with the non-activated sample the value of ΔE is 1.43 times lower. In addition, the increase of the radon release rate in the time between 100 and 200 minutes is much more pronounced with the activated sample

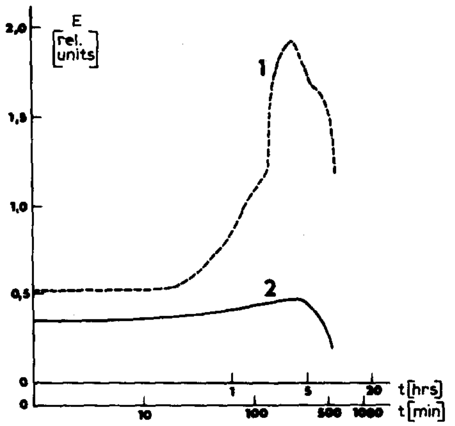

Fig. 5. ETA curves of C_3S hydration at the temperature of 25 °C /C_3S was mixed with water in the ratio water/solid = = 0.4/. The C_3S samples C_1 and C_2, resp. of the equal surface area $S = 0.4\ m^2\ g^{-1}$ were thermally activated by heating to 600 °C in air /curve 1/ and used for the hydration without activation /curve 2/.

/curve 1/ when compared to the non-activated one /curve 2/. The break on the curve 1 in Fig. 5 occurs somewhat earlier than on the curve 2. The reason for the described behaviour is following: during the heating and subsequent rapid cooling of C_3S the activation of existing centers takes place and even new centers in the surface and structure of the solid are formed which act as the most reactive sites for the interaction of C_3S with water.

Effect of organic admixtures. The decelerating effect of sugars on the C_3S hydration is well known. But it was of interest to ascertain how this effect is reflected on the ETA curves. Fig. 6 shows the ETA curves of C_3S-water suspensions where to the sample C_1 water without any admixtures /curve 1/ and water with 0.1 % of xylose /curve 2/ was added. The addition of 0,1 % of xylose to water is reflected by a slowing down of the velocity of the initial interaction of C_3S with water. The parameter ΔE characterizing the hydration velocity is $\Delta E = 0.773$ for the suspension without any admixtures and $\Delta E = 0.539$ for the suspension containing 0.1 % of xylose.

In Table 1 we summarize the values of the ΔE parameter characterizing the C_3S-water interaction between 10 and 100 minutes after the mixing with water, and other characteristics of the system studied.

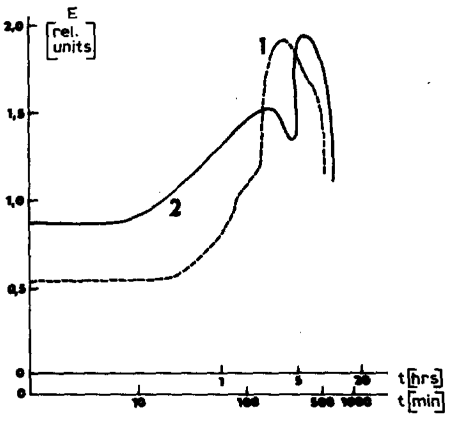

Fig. 6. ETA curves of C_3S hydration at the temperature of 25 °C in distilled water /curve 1/ and in water containing 0.1 % of xylose /curve 2/. The C_3S sample C_1 was thermally activated /cf. Fig. 5, curve 1/.

TABLE 1
Characteristics of the C_3S-water suspensions

Characteristics of solid C_3S		Hydration solution	Characteristics of the C_3S-water interaction, ΔE
Sample notation	Surface area $m^2\,g^{-1}$		
Sample A	0.3	distilled water	0.154
Sample B	1.2	distilled water	0.485
Sample C_1 non-activated	0.4	distilled water	0.055
Sample C_2 thermally activated	0.4	distilled water	0.773
Sample C_2 thermally activated	0.4	0.1 % water solution of xylose	0.539

By comparing the ΔE values in Table 1 we can draw the following conclusions:

- the higher is the surface area of the C_3S sample the higher is also the velocity of the interaction
- the thermal activation of the C_3S sample enhances the velocity of its interaction with water
- the presence of 0.1 % of xylose in the water leads to the slowing down of the velocity of C_3S-water interaction

The confirmation of the generally known dependences of the C_3S reactivity approves the applicability of the ETA and that of the parameter ΔE in this study.

Effect of temperature. The investigation of the hydration process in conditions of the elevated temperature can be made by means of a few methods only, among them emanation thermal analysis. Fig. 7 shows the ETA results of the C_3S-hydration, measured isothermally at 25 and 35 °C, resp.

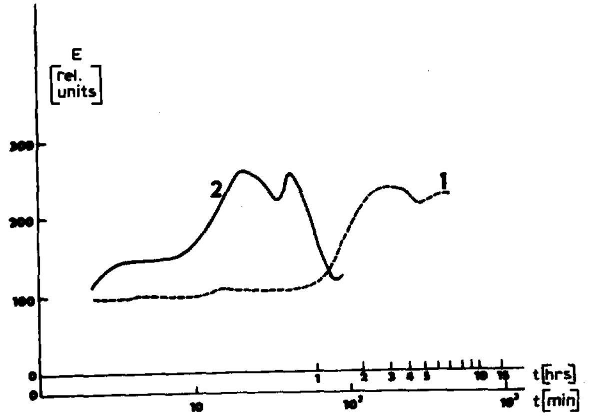

Fig. 7. ETA curves of C3S hydration at the temperature of 25 °C /curve 1/ and 35 °C /curve 2/.
C_3S was mixed with water in the ratio water/solid = = 0.4.

The difference in the curves in Fig. 7 reflects the influence of the temperature on the hydration of C_3S. The induction period of hydration is considerably shortened when the hydration takes place at 35 °C, in comparison to the hydration at 25 °C. The higher temperature enhances the accelerated hydration period. Nevertheless, both of the ETA curves, corresponding to the hydration at 25 and 35 °C, resp. exhibit analogical effects in the subsequent hydration stage, which confirm the viewpoint of the similarity of the structure of hydration products formed. The effects on the ETA curve are due to the changes of microstructure of the hydration products, namely of the microporosity.

Hydration of cement

Comparison of ETA results with results of commonly used methods. Fig. 8 shows the results of the study of portland cement hydration at 20 °C; water/ /cement ratio = 0.3. The ETA curve /1/ is compared with the results of measurements of the penetration resistance /2/ and calorimetry /3/ of the cement paste.

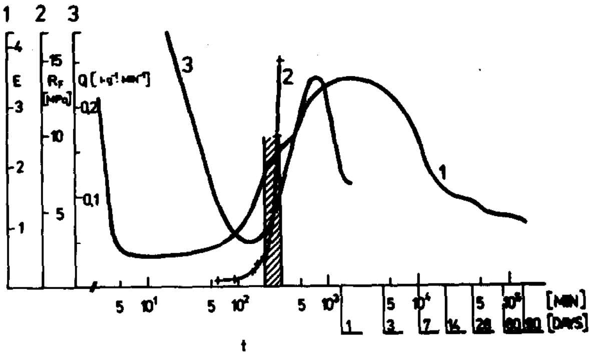

Fig. 8. Comparison of time dependences of the parameters measured during the hydration of portland cement at the temperature of 20 °C; water/ /cement = 0.3:
curve 1 - radon release rate /ETA/;
curve 2 - penetration resistance;
curve 3 - rate of liberation of hydration heat /calorimetric curve/.
The setting of the cement paste determined by the standard Vicat test is marked by hatching.

The ETA curve reflects clearly the stages of the cement hydration /ref. 1/: the initial hydration, the induction period, the accelerated period and the final period where the hydration is controlled by the diffusion of water through the hydrated products.

On mixing cement with water, the radon release rate of the sample rapidly increases and, after several minutes it decreases /curve 1/. The sudden increase of E indicates the first interaction of the surface of cement grains with water, whereas the rapid decrease indicates the formation of a layer of hydration products which results in the slowing down of the rate of initial hydration. This layer is of low permeability not only for water molecules but also for radon atoms as indicators of the structure changes of the cement paste.

The next interval, called the induction period, is characterized by constant, relatively low values of E indicating that hydration has practically stopped. The reactivation of the hydration process connected with the penetration of water into the unreacted cement grains is characterized by an increase of the radon release rate. Initially E is assumed to be proportional to the hydration rate, but later, the hydration products limit the rate at which radon atoms can escape from the point at which reaction occurs. Further changes on the ETA curve /curve 1, Fig. 8/ of the cement paste sample can be ascribed mainly to the processes taking place in the hydration products.

In the period of the accelerated hydration ETA can be used for the study of the kinetics of cement hydration. ETA enables us to distinguish the end of the induction period more precisely than any of the methods commonly used for the study of the cement hydration. The onset of the increase of E /curve 1, Fig. 8/ which indicates the end of the induction period, appears earlier than the heat evolution effect by the calorimetry /curve 3, Fig. 8/. This is due to the physico-chemical principles of the respective methods: ETA indicates the changes taking place in the surface layer of the cement grains, which is radioactively labelled, whereas calorimetry reflects the overall effect of all hydration reactions taking place in the bulk of the sample.

The changes in the penetration resistance /curve 2, Fig. 8/ corroborate the ETA results. From the curve 2, Fig. 8, it is evident that the rise of the penetration resistance is closely connected with the increase of the radon release rate E. The onset of the rise of penetration resistance fits well with the inflection of the ETA curve.

As it can be seen from the results of ETA mentioned above, the theroretical model of the radon release from porous solids agrees well with the experiments. The changes in the radon release rate E indicate both changes of surface area and changes of porosity: gel pore size may range from a diameter of 0.1 to 1 nm, the diameter of radon atom is 0.4 nm. The changes of the gel pores in the hardened cement paste caused by saturating the sample with water and subsequent drying, are indicated very clearly by the change of radon release rate /ref. 10,11/.

Cement hydration at elevated temperatures. It was shown in the study of C_3S hydration that ETA can be advantageously used for investigating hydration under various conditions. Fig. 9 shows the results of the cement paste during hydration at isothermal conditions of 85 °C /curve 1/, 45 °C /curve 2/, and 35 °C /curve 3/. The form of the ETA curves in Fig. 9 reflects the known fact that the structure changes occuring during the cement paste setting are accelerated at elevated temperatures.

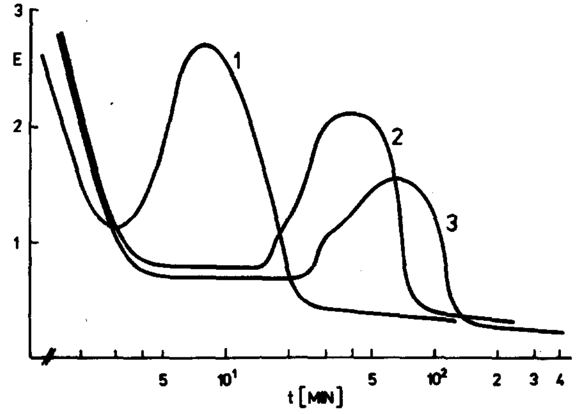

Fig. 9. ETA curves of the portland cement hydration ; water/cement = 0.3, the temperatures of the hydration are:
85 °C /curve 1/,
45 °C /curve 2/, and
35 °C /curve 3/.

The apparatus gives the possibility of modelling the respective technological temperature conditions. The advantage of this method consists in the possibility of investigating the evolution of the hardened cement paste structure continuously and in an automatic regime. The results obtained by ETA can be used not only for the characterization of the evolution of hardened cement paste structure but also for the evaluation of various cements from the viewpoint of temperature influence on their hydration /ref. 11,12/.

Effect of the presence of admixtures. The ETA has been also used for investigating the influence of gypsum concentration on the cement hydration /ref. 10/. The influence of admixtures on the cement hydration both in the cement powder and/or in water can be advantageously studied by ETA.

In this way the effect of a large number of inorganic and organic admixtures of the cement hydration can be investigated. Information about the end of the induction period and the intensity of the accelerated hydration period can be obtained from ETA results. Furthermore the changes in the microstructure of the cement paste during setting and hardening can be followed continuously in the required conditions, by this method.

CONCLUSION

The emanation thermal analysis has been demonstrated as a powerfull tool in the study of the hydration of cement and clinker minerals. This method makes it possible to assess especially the early stages of the cement paste setting.

A method based on ETA for the evaluation of the velocity of interaction between C_3S /and other clinker minerals/ and water at the early hydration stage, has been suggested. It can be used for the study of the kinetics of the early hydration stage.

The ETA offers new insights into the development of the microstructure of hydrated cementitious materials. This method can be advantageously applied to the investigation of the secondary changes in the cement hydration products, to that of the influence of additives, temperature and other factors on the hydration.

The method of ETA possesses several methodical advantages in comparison with commonly used methods. The ETA enables us to follow the processes of the cement hydration continuously and under specified conditions of temperature, humidity, gas medium, etc. This is a great advantage of the ETA in comparison with other methods, where the hydration has to be stopped e.g. by drying, evacuation or freezing. These procedures might substantially change the structure, the surface area and the porosity of the sample.

The ETA can be applied in plant laboratories for the operative checking of cement samples from the viewpoint of the velocity of the initial stage of cement hydration and subsequent processes which control the resulting mechanical properties of hardened cement paste.

The large field of the application of ETA can be found also in special, non-building, technologies, e.g. in the investigation of fixation of radioactive waste by cementation, where especially the effects of the presence of admixtures, the durability of the hardened cement paste towards aggresive media and temperature are of interest. A method giving the possibility of the evaluation of the durability of the hardened cement paste and other building materials, based on the ETA application, has been suggested /ref. 13/ and successfully approved in the praxis.

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