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THEORY OF EMANATION THERMAL ANALYSIS
X. Characterization of morphology changes during hydration of cementitious binders

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Abstract

Computer modelling of time dependences of radon release rate during hydration of $3CaO{\cdot}SiO_2$ was carried out. It was demonstrated that the emanation thermal analysis (ETA) can be used for the characterisation of morphology changes during hydration of Portland cement clinker minerals. The presence of various additives and increased temperature affecting kinetics of hydration were simulated by the mathematical model of the radon release rate during hydration of $3CaO{\cdot}SiO_2$. A good agreement between the mathematical model and ETA experimental results was found.

Keywords: emanation thermal analysis, hydration, mathematical modeling, morphology changes, tricalcium silicate

Introduction

Emanation thermal analysis (ETA) [1–3] has been already recommended as the method making possible to obtain information about the kinetics of morphology changes and behaviour of Portland cements and other hydraulic binders during their hydration at various temperatures, as well as during the storage of the cemented waste products under conditions of varying humidity [4–6]. There is a need to understand the mechanism and kinetics of processes controlling the development of mechanical properties of the calcium silicate containing hydraulic binders more deeply. ETA can be a useful tool to obtain the requested information.

The aim of this paper is to show the suitability of ETA application for characterisation of morphology and surface area changes during hydration of tricalcium silicate $3CaO{\cdot}SiO_2$ (C_3S) as a component of cement clinker. The sensitivity of ETA curves to hydration temperature, different surface area of the C_3S and the presence of admixtures affecting the kinetics of the hydration process is demonstrated in the paper.

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Background for emanation thermal analysis application

ETA is based on the measurement of the release of radon from previously labelled materials. The changes in the radon release rate reflect changes in the surface area and microstructure of the previously labelled samples. For labelling samples by radon atoms the incorporation of trace amounts of the radionuclides ^{228}Th and ^{224}Ra by adsorption from solution is used. Radon atoms are formed as a result of spontaneous radioactive decay according to the scheme

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

By using ^{228}Th (half-life is 1.9 years) as the parent radionuclide, a practically permanent source of ^{220}Rn is incorporated into the sample which makes it possible to investigate even the long lasting processes.

Radon release is controlled by the diffusion of radon in the solid material and by the recoil due to the energy, which every radon-atom gains during its formation from the atoms of radium. The scheme of hydrating surface of C_3S grain labelled with radio nuclides of ^{228}Th, ^{224}Ra and ^{220}Rn is presented in Fig. 1.

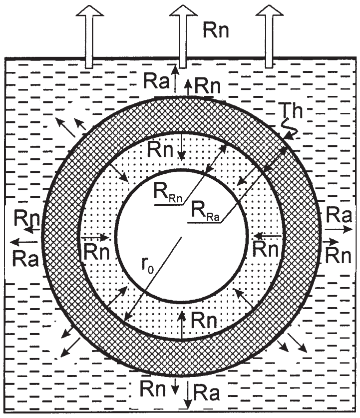

Fig. 1 Schematic drawing of the hydrating surface of $3CaO{\cdot}SiO_2$ (C_3S) grain, labelled with ^{228}Th, ^{224}Ra and ^{220}Rn

It was demonstrated by many experimental works and by theoretical considerations [1] that the rate of the radon release atoms from a solid depends on the structure changes which may take place in the solid or on its surface. Consequently, processes taking place in the solids and on their surface can be investigated by means of ETA. The increase of radon release rate *E* indicates the increase of the surface area, whereas the decrease of radon release rate reflects a closing pores and decrease of surface area. It should be mentioned that porosity changes in the nanometer scale comparable to the radon atom size i.e. 0.38 nm can be investigated, under ‘in situ’ conditions of the sample treatment of ETA.

Model of radon release from hydrating sample considering interface and diffusivity changes due to hydration

A two-phase (solid–water) system

A mathematical model of the release of inert gas from a two-phase system considering changing solid-particle surfaces and diffusivity changes was developed by Balek and Kří [7]. Time dependences of the radon release rate (called here ETA curves) under the assumption of the Pommersheim–Clifton [8] of hydration kinetics were simulated by computer using this model. A good agreement of the simulated ETA curve with experimental results was found for the hydration of powdered tricalcium silicate [9].

The Balek–Kří model [7] (called here BK model) was designed under following considerations:

- A solid material in the form of a collection of spherical grains, the radii of which are distributed according to some functions, which are in contact with a reacting fluid phase filling all the space between the grains.
- The surfaces of the grains are impregnated by ^{228}Th, which decays to intermediary nuclide, ^{224}Ra; ^{224}Ra decays to an inert radioactive gas, ^{220}Rn, which is, in the case of compact solid grains and a low temperature, released from the grain almost exclusively by recoil, after which it is transported by diffusion through the liquid phase in the pores and is measured on the surface of the sample (see the schematic drawing in Fig. 1). The negligible concentration of the sample warrants the assumption that neither their presence nor their decaying process influence the course of the main physico-chemical processes in the system.
- The porous space filled by the liquid phase to be a diffusion quasicontinuum (the quasicontinuum-domain model [7]), the value of the main diffusion coefficient depending on the degree of the reaction and, thus, on time. The only free surface for the final transport of the radon is the surface of the sample above it, so that the only statistically important gradient of the measured gas concentration exists in the direction vertical to the sample surface. The formation of the radon in the quasicontinuum by its emission from the grains can be a source function which depends exclusively on time.
- The emerging surface is formed out of the near-to-surface inner layers by their diffusion controlled reaction with the fluid phase. In this case, the atoms of the intermediary radionuclide as well as those of the radioactive inert gas which have not decayed up to the surface by the α-decay reaction and are thus available directly for the diffusion in the porous quasicontinuum. There should exist some critical degree of the overall reaction, at which virtually all these atoms are, effectively, on the surface or decayed. In such a way, the ongoing reaction enhances the value the recoil emanation rate from the grain up to the critical degree of the reaction.

The space between the grains is filled progressively by the newly formed material, which can trap the radon atoms emitted by recoil and thus lower the effective value of the emanation rate. The time dependence of the source function value (or the recoil emanation rate) is a transformation of the time dependence of the reaction degree, which has to be established for the individual reaction process. The time dependence of the reaction degree has to be found from an experimental study of the reaction kinetics.

- The diffusion of radon through the solid reactant as well as through the solid reaction product is considered negligible, relatively to the diffusion through the quasicontinuum. If the relatively impermeable product covers the surface of the solid grains and thus fills the space between the grains, the Knudsen diffusion coefficient has to decrease progressively with the increasing reaction degree.
- The spherical grain of the tricalcium silicate (C_3S) is supposed to react with water in a spherical zone proceeding from the outer layer of the secondary hydrate. In this way we can expect that in the early hydration stage an increase of surface area of the hydration products will be reflected by the increase of the radon release rate, due to recoil. On further stages of the hydration where the densification of amorphous C–S–H hydration products and their crystallisation is supposed, a decrease of the radon release rate, due to recoil and diffusion in the opened pores resulted.
- Radon is transported through the outer surface of the sample either by pore diffusion from inner layers of the sample or by recoil from the surface layer of it. Consequently, the model curves simulating the radon release during hydration of C_3S, under assumption of the BK model, demonstrated the increase of emanation rate *E* at the very beginning of the hydration, followed by the decrease of *E*.

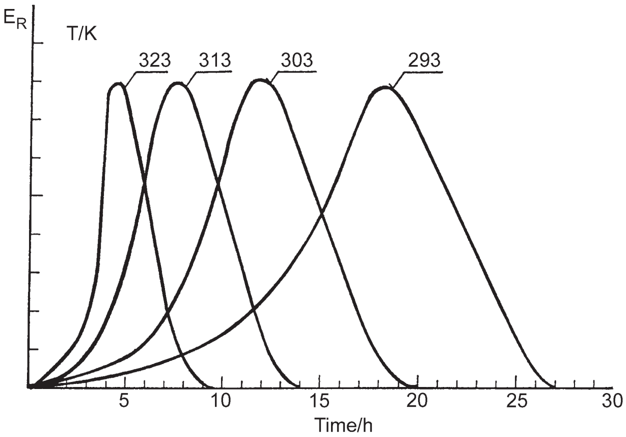

Fig. 2 Simulation curves of the emanation rate during hydration of C_3S at various temperatures (20–50°C, i.e. 293–323 K); for other parameters see text

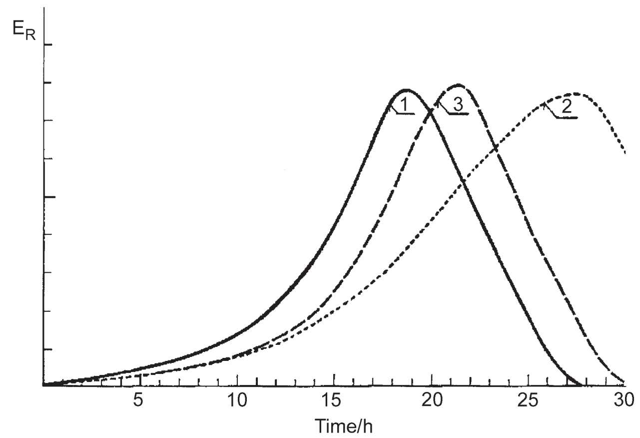

Fig. 3 Simulation curves of the emanation rate during hydration of C_3S at 293 K supposing various concentrations Ca^{2+} (curve 2 corresponds to the concentration five fold lower than the concentration presented by curve 1, curve 3 corresponds to the case of the increased concentration of Ca^{2+} due to hydrolysis of C_3S; for detailed description see the text)

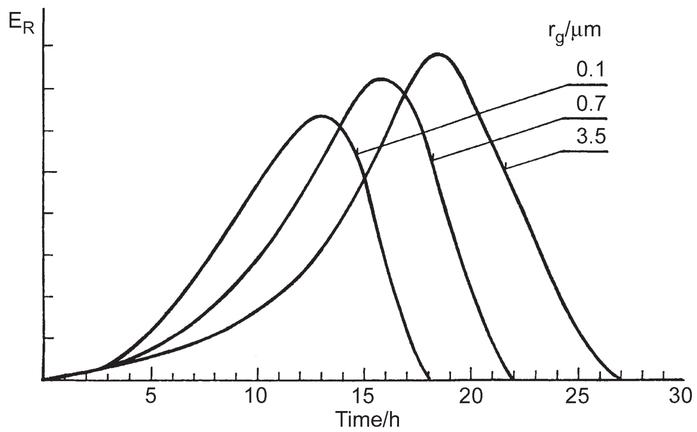

Fig. 4 Simulated curves of the emanation rate during hydration of $3CaO{\cdot}SiO_2$ supposing various grain size (0.1, 0.7 and 3.5 µm) at temperature of 293 K

Results of the computer modelling presented in Figs 2–4 reflected the ability of ETA the reveal changes in the morphology of the hydration samples. The diffusion equations used in the mathematical modelling were solved by numerical methods (using a modified Rudge–Knutt method).

For the simulations of the emanation rate from hydrated calcium silicate ($3CaO{\cdot}SiO_2$), the following initial values of the parameters have been used: $w/s=1.0$, $a_1=1.0$, $\gamma=3.2$, $\nu=2.2$, $D_{i0}=1.35\cdot10^{-5}$ m^2 s^{-1}, $Q_D=40$ kJ mol^{-1}, $D_{x0}=0.82\cdot10^{-5}$ m, $Q_{dx}=$

45 kJ mol^{-1}, D_∞=$2.23\cdot10^{-5}$, Q_{D0}=30 kJ mol^{-1}, x_0=$3.5\cdot10^{-8}$ m, β_0=$0.6\cdot10^8$, Q_β= 40 kJ mol^{-1}, K_0=8.1, Q_K=40 kJ mol^{-1}, r_g=$3.5\cdot10^{-6}$ m, c_0=0.1 mol l^{-1}, T=293 K, δ_1=5.0, δ_2=2.0, δ_3=5.0; where w/s is the ratio of water to the original silicate; a_1 is the number of water molecules needed for the hydration of one molecule of the silicate; γ being the specific mass; ν is the normalising factor; D_i, D_0 and D_x are the diffusion coefficients of water in the original silicate, in the secondary and in the primary hydrate, respectively; D_∞ is final value of the diffusion coefficient of radon, corresponding to the porosity of the product; Q is activation energy; K is the rate constant of the primary hydration; x_0 is the thickness of the primary layer at the very start of the reaction, β is the rate constant of its disappearing; r_g is the initial grain radius; c_0 is the concentration of the free ions of calcium or equivalent metal in the solution; T is experiment temperature; δ_1, δ_2 and δ_3 are empirical coefficients to be found for given process.

In Figs 2–4 the values of the emanation rate E_R are given in relative (non-dimensional) units.

Figure 2 shows the simulated curves of time dependences of emanation values E_R for the cases of different temperatures, namely, 293, 303, 313 and 323 K, respectively. In accordance with the experimental data, the maximum of the curves moves markedly to a shorter reaction time and its half-width decreases at higher reaction temperature. The effect the change of the starting concentration of the Ca^{2+} ion in the liquid phase on ETA curve can be seen in Fig. 3. As it follows from the comparison of curve 2 and curve 1, the concentration decreased of Ca^{2+} ions by factor of 5 brought about a marked change of the shape of the curve, as well as a shift of its maximum to a longer reaction time. Curve 3 in Fig. 3 reflects the case of the reaction suppression by some chelating agents and its agitation by using the ion-rich solutions as the original liquid phase.

In addition, we have investigated the effect of grain size of original C_3S on ETA curves, characterizing a hydration process. In the simulations shown so far, a uniform

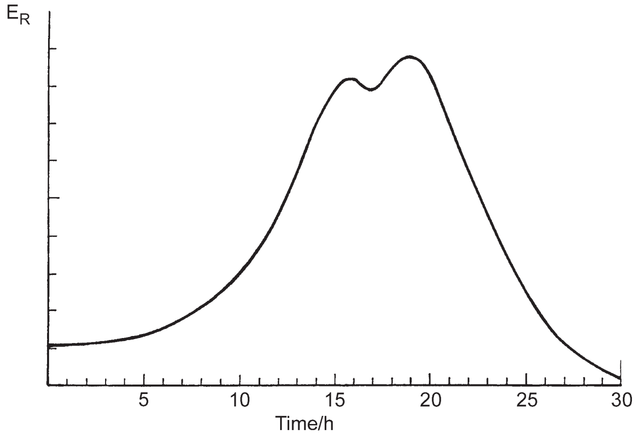

Fig. 5 Simulated curve of the emanation rate measured during hydration of $3CaO\cdot SiO_2$ at 293 K (w/solid=0.4) supposing a two-sized calcium silicate sample (grain sizes 0.7 and 3.5 μm)

distribution of the grain size has been assumed. In real samples, however, this condition can hardly be fulfilled. Therefore, it is important to explore the change of the emanation rate curve with the varying grain size. This was simulated for the grain radii 0.1, 0.7 and 3.5 μm. As it follows from Fig. 4, the shift of the curve maximum to a shorter reaction time with the decreasing r_g was observed. The simulated ETA curve characterizing the hydration of two sized C_3S sample (grain sizes 0.7 and 3.5 μm) is demonstrated in Fig. 5.

Thus, we should take into account that the history of the samples studied may strongly influence the kinetics of their hydration. The differences in the microstructure development of hydrated products can be characterized by ETA curves measured under ‘in situ’ conditions of the hydration.

Three components model of the hydration supposing formation of an intermediate metastable phase on the grain surface

The BK model [7], successfully used for simulating time dependencies of the radon release rate from the tricalcium silicate suspension, was found too complex to be used in the direct evaluation of the ETA experimental results. Therefore, we have developed an updated ‘three components model’. Its main advantage is the simplicity. In this model we have considered the formation of intermediate metastable hydration products, which are transformed into final hydration products.

The model takes into account that the formation and growth of amorphous hydration products takes place in the early hydration of C_3S. On the other hand, the ‘two phase BK model’ is more suitable for the description of the radon mobility during further hydration stages involving densification of the hydrated layers, etc.

In the ‘three components model’ we have supposed that the intermediate metastable phase is being formed on the surface of the grains of the initial phase.

In this paper we introduce parameters useful for the characterization of the state of an interspersion of phases involving phases denoted 1, 2 and 3 resp. The interspersion can be characterized as the set of volume fractions α_1, α_2 and α_3 of the phases ($\alpha_1+\alpha_2+\alpha_3=1$).

Following considerations were supposed in the mathematical modelling of hydration process by means of the ‘three components model’, sample labelling by radionunclides of ^{228}Th and ^{224}Ra, the random nucleation of the newly formed phases (resulting in the first order reaction kinetics).

Following parameters were introduced in the modelling radon release rate: L- the thickness of sample, E – emanation rate of the sample, D_1, D_2 and D_3 – are the radon diffusion coefficients in the initial final and intermediate solid state phases denoted by numbers 1, 2 and 3, resp. ($D_3>>D_1$ and $D_3>>D_2$).

In the frame of the parallel diffusion mechanisms we have supposed that the total value of the emanation rate of the sample is composed by the sum of the emanation rate values of individual phases 1, 2 and 3.

In the conditions of the isothermal solid state reaction we can write

$$E(t)=E_1\alpha_1(t)+E_2\alpha_2(t)+E_3\alpha_3(t) \tag{2}$$

The emanation rate of the slab-like sample can be expressed as follows

$$E_{\mathrm{i}}=\frac{1}{L}\left(\frac{D_{\mathrm{i}}}{\lambda}\right)^{1/2}\mathrm{th}L\left(\frac{\lambda}{D_{\mathrm{i}}}\right)^{1/2} \tag{3}$$

where λ is the radioactive decay constant of radon, D_{i} is the radon diffusion coefficient in an individual phase i of the solid sample.

The temperature dependence of the radon diffusion coefficient can be written as follows, considering Arrhenius law

$$D=D_0\exp-\frac{Q}{RT} \tag{4}$$

where Q is the activation energy of radon diffusion in the respective solid phase, D_0 is the pre-exponential factor characterizing the respective lattice property, T is the temperature.

During the random nucleation the time dependence of the decrease of the amount of the phase 2 is determined by the integral Gauss distribution curve

$$\alpha_2(t)=erfz=\frac{2}{\pi^{1/2}}\int_0^z\exp(-t^2)\mathrm{d}t \tag{5}$$

where the increase in the amount of the phase 2 can be written as

$$\alpha_1(t)=1-a_2(t)=erfcz=1-erfz \tag{6}$$

The time dependence of the phase 3 amount is expressed by the differential Gauss distribution curve

$$\alpha_3(t)=A\frac{\mathrm{d}(\alpha_2(Kt-\tau_0))}{\mathrm{d}t} \tag{7}$$

where A is the amount of elemental crystallographic cells of the intermediate phase 3, which are formed after the disappearance of the elemental cell of the initial phase 1. This parameter determines the height of the curve corresponding to the function $\alpha_3(t)$; K is the equilibrium constant of the chemical reaction underlying the formation of the intermediate phase 3, it can be expressed as the ratio $K=k_{\mathrm{form}}/k_{\mathrm{transform}}$ where k_{form} is the rate constant of the intermediate phase 3 formation, $k_{\mathrm{transform}}$ is the rate constant of its transformation into the final phase 2. The equilibrium constant K determines the height of the function, representing $\alpha_3(t)$, which reflects the intensity of the solid state transformation; τ_0 is the parameter determining the position of the $\alpha_3(t)$ function of the time axis.

The calculations made by Eqs (5), (6) and (7) enabled us to obtain time dependences of the concentrations of the initial, final and intermediate phases, resp. As it follows from Fig. 6, the amount of the initial phase monotonously decreased from 1 to 0 (curve 1) whereas the amount of the final phase increased from 0 to 1 (curve 2). The time dependence of the amount of the intermediate metastable phase 3 is described by a peak-like curve (curve 3). Using Eq. (2) and taking into account Eqs (3), (4) and (5) a peak-like ETA curve resulted from the model (Fig. 6, curve 4). In ETA curve modelling we have supposed that the solid sample was labelled by the radionuclides of ^{228}Th and ^{224}Ra representing a quasi-permanent source of radon ^{220}Rn atoms.

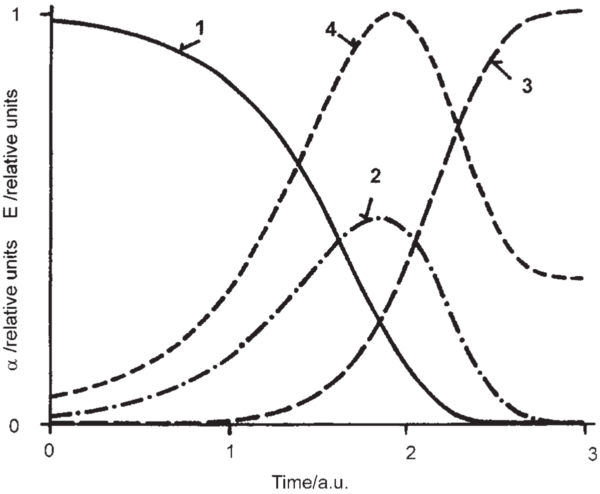

Fig. 6 Time dependences of the concentrations of individual phases 1, 2 and 3 (curves 1, 2 and 3, resp.) involved in the 'three components model' of hydration. The theoretical ETA curve calculated by means of the model is given as curve 3

Following parameters characterising the properties of the phases decomposition reaction were considered: E_1=0.02, E_2=1, E_3=0.2. It means that the value E_3 of the intermediate metastable phase was 50 times higher than the E_1 value corresponding to the initial phase, and 5 times higher than the value E_2 corresponding to the final reaction product. The calculations were carried out considering the following parameters of the hydration reaction A=0.25, K=τ_0=2.2. The isothermal conditions of the thermal decomposition were considered. These parameters correspond to the real experiment, as the intermediate phase possesses much higher disorder degree than the initial and final phases.

Table 1 Values of emanation rate E considered for individual phases 1, 2 and 3 in the modelling ETA curves

Curve No.	E_1	E_2	E_3
1	1	1	1
2	1	1	0.1
3	0.1	0.1	1
4	1	0.1	1
5	0.2	1	0.02
6	0.2	1	0.2

Moreover, we have used this ‘three components model’ for simulating time dependences of the radon release rate during solid state reactions where the components of the reaction differed in the values of emanation rate E_1, E_2 and E_3 resp. (Table 1). As it follows from the results of the modelling presented in Fig. 7 the time dependences of the total emanation rate of the sample can differ in the shape, even when the parameters, characterising the kinetics of the chemical reaction are equal.

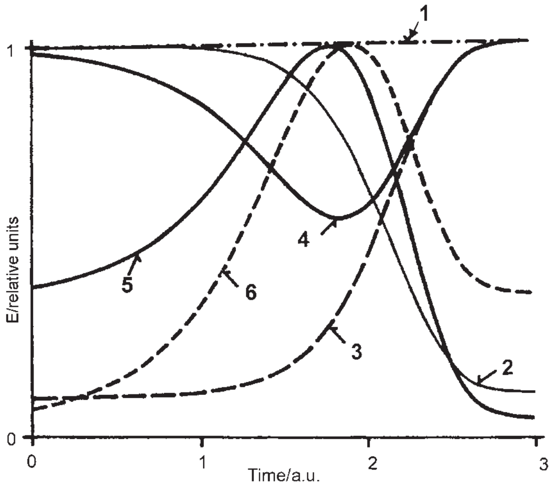

Fig. 7 Results of the modelling ETA curves characterizing morphology changes on solid state processes at constant temperature. The ‘three components model’ was used in the modelling, the values of emanation rate of individual phases 1, 2 and 3 are given in Table 1 as E_1, E_2 and E_3

To understand these results, it should be mentioned that the shape of ETA model curves obtained by the mathematical modelling and presented in Fig. 7 depends on

(i) the values of the emanation rate of the phases present in the sample, E_1, E_2 and E_3, which, in their turn, depend on the values of the radon diffusion coefficient corresponding to the respective phases;

(ii) on the rate constant of the thermal decomposition reaction;

(iii) on the amount of the elementary crystallographic cells formed as the result of the disappearance of the initial phase;

(iv) and other parameters characteriszing the hydration process.

Consequently, by using the ‘three components model’ the simulated ETA results can reveal the presence of intermediate metastable phases during solid state reaction as well as the dynamics of its formation from the initial phase and transformation into the final phase.

In this way it was demonstrated that the emanation thermal analysis is sensitive enough to the changes in the microstructure of the sample, taking place as a result of the hydration of hydraulic binders. This approach enabled us to consider different morphology for the reaction intermediate products with regard to the initial solid sample and final reaction products (as characterized by the emanation rate values).

Conclusions

ETA can be proposed as a powerful tool in the study of the hydration of Portland cement and clinker minerals. This method makes it possible to assess especially the hydration process. 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 of the influence of additives, temperature and other factors on the hydration. The hydration process can be characterized under ‘in situ’ conditions of selected temperature, humidity, gas medium, etc. This is a great advantage in comparison with other methods, where the hydration has to be stopped in order to characterize the surface area of the hydrating phases.

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