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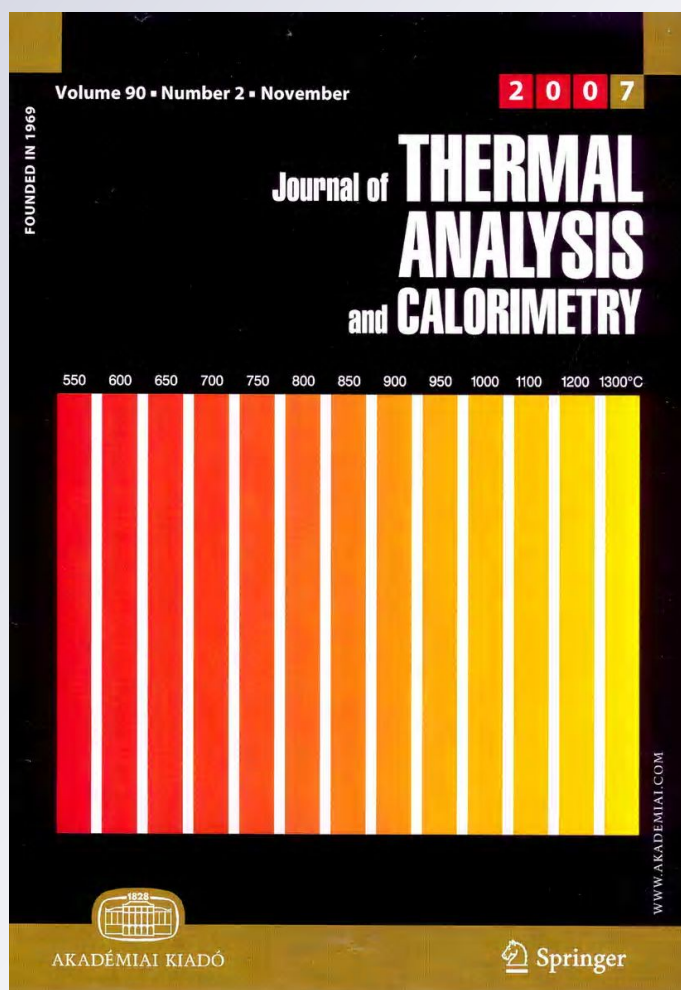
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Hydration of tricalciumsilicate (Ca_3SiO_5) investigated by emanation thermal analysis

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Abstract The method of emanation thermal analysis (ETA), based on the measurement of radon release from samples, has been used in the investigation of the tricalcium-silicate (Ca_3SiO_5) to characterize the microstructure development during the sample hydration. Results of the ETA made it possible to obtain the diffusion structural diagnostics of the material under in situ conditions of its hydration. The influence of temperature and surface area of the tricalcium-silicate sample on kinetics of the sample hydration was characterized. Computer modeling of time dependences of radon release rate during hydration of tricalcium-silicate was carried out. A good agreement of the numerical model with the experimental results of the radon release was found.

Keywords Emanation thermal analysis · Hydration · Microstructure · Tricalcium-silicate · Radon migration

Introduction

From the studies of cement binders hydration, it is obvious that the information about microstructure changes during

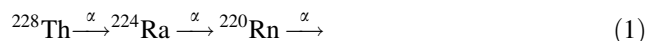
first hour of their hydration is of great practical importance. Various methods have been used to characterize the hydration of cement binders and their components including tricalcium-silicate as the main component of the cement binder [1–3]. The emanation thermal analysis (ETA), based on the measurement of radon incorporated into the samples, has been already recommended to obtain information about the kinetics of morphology changes and behavior of Portland cement during hydration [4, 5].

In this study, the ETA has been applied to characterize the morphology development during hydration of tricalcium-silicate (Ca_3SiO_5) as a component of the cement clinker. The results of computer modeling of time dependences of the radon release rate during hydration of tricalcium-silicate are compared with the corresponding experimental results obtained.

Experimental

ETA

The ETA method is based on the measurement of radon released from the labeled samples [5–8]. Radon atoms do not react with the solids in which they are incorporated in trace amount. For labeling samples by radon atoms, the incorporation of trace amounts of the radionuclides ^{228}Th and ^{224}Ra by adsorption from a solution was used. Radon atoms are formed as a result of the spontaneous α -radioactive decay according to the scheme



By using ^{228}Th (half-life 1.9 years) as the parent radionuclide a practically permanent source of ^{220}Rn (half-life 55.8 s) was incorporated into the sample.

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The release of radon atoms is controlled by the diffusion in the solid and by the recoil energy which every ^{220}Rn atom gains during its formation from the atoms of radium ^{224}Ra .

The relative value of the radon release rate, E , from the sample depends on surface area and the radon diffusion coefficient in the solid.

The radon release rate, E , of the sample can be expressed as follows:

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

where S_{eff} is the effective surface area related to the mass of the sample, K_1 and K_2 are constants, D is the radon diffusion coefficient in a solid, ρ is the density of the solid and λ is the ^{220}Rn radon decay constant ($\lambda = 0.0127 \text{ s}^{-1}$).

Moreover, the rate of the release of radon atoms from a solid depends on the structure changes or chemical processes which take place in the solid or on its surface.

Samples

Samples of tricalcium-silicate (Ca_3SiO_5) studied were prepared by high temperature synthesis and subsequent grinding. The surface area values of the investigated samples are $0.3 \text{ m}^2/\text{g}$ (sample A) and $1.2 \text{ m}^2/\text{g}$ (sample B). Four weeks prior hydration the powdered samples were labeled by an impregnation technique by using ^{228}Th and ^{224}Ra nuclides [5–8].

The samples were labeled by impregnation with the acetone solution containing ^{228}Th and ^{224}Ra in the concentration of the order of $10^5 \text{ s}^{-1} \text{ cm}^{-3}$, subsequently, the acetone solvent was evaporated. The atoms of ^{220}Rn were incorporated to a maximum depth of 120 nm as a consequence of the recoil energy 85 keV/atom which every atom gains during the α -decay of its parent radionuclides [6–10].

The specific radioactivity of the samples was 10^5 Bq/g . The labeled samples were stored in dry conditions at least 4 weeks before the measurements to allow the radioactive equilibrium between the ^{228}Th and ^{224}Ra nuclides to be established. The atoms of radon, ^{220}Rn , were formed by the spontaneous α -decay of ^{228}Th and ^{224}Ra , as described by the Eq. 1. The samples of the water suspensions of the tricalcium-silicate were prepared by the addition of water to the solid labeled samples in the water/solid ratio $w/s = 0.4$.

Measurements of samples

The samples in an amount of about 3 g were homogenized by mixing and put in a PVC vessel into the measuring device. During the ETA measurements, the samples were kept at a constant temperature of 25 and 35 °C, respectively. An air saturated with water vapor (relative humidity

of 95–3%) was used as a gas medium for the ETA measurements. The high relative humidity protected the sample from drying out during the experiment.

An equipment produced by NETZSCH Ltd., Selb, Germany in cooperation with the Nuclear Research Institute Řež, plc, Czech Republic was used for the ETA measurements.

The radon release rate, E , are presented (in relative units) as $E = A_\alpha/A_{\text{total}}$, where A_α is α -radioactivity of radon released in unit time from the sample, and A_{total} is the total γ -radioactivity of the labeled sample. The A_{total} value is proportional to the rate of radon formation in the sample. Semiconductor and NaI(Tl) detectors were used for the α - and γ -radioactivity measurements, respectively.

Results and discussion

Hydration of tricalcium-silicate (Ca_3SiO_5)

Figure 1 depicts the time dependence of the radon release rate from the (Ca_3SiO_5)-water sample measured isothermally at 25 °C. It is assumed that after mixing the Ca_3SiO_5 with water the hydration reactions take place.

We supposed that during the hydration the labeled (Ca_3SiO_5) layers gradually changed into the calcium silicate hydrated products. The effects observed by the time dependence of the radon release rate indicate the changes of the microstructure of the hydrated products, namely the surface area and the size of micropores.

It followed from the ETA results that in the first 200 min after mixing the Ca_3SiO_5 with water the hydration process took place in the (Ca_3SiO_5) sample.

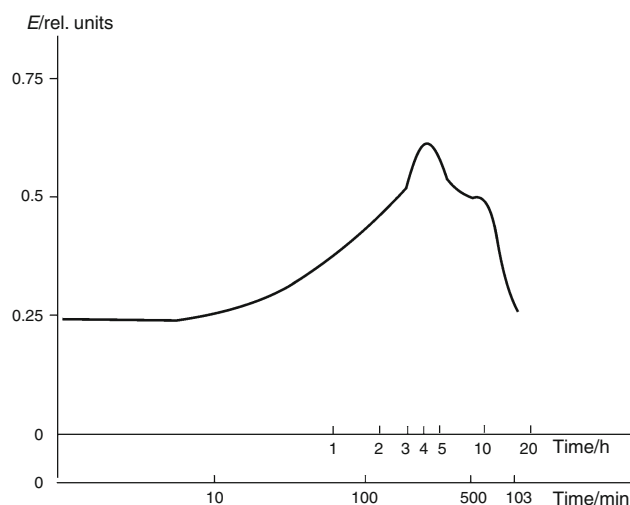


Fig. 1 Time dependence of the radon release rate, E , measured by ETA during the hydration of tricalcium-silicate at the temperature of 25 °C. The water/solid ratio was $w/s = 0.4$

In the subsequent time interval values of the radon release rate, E , reflected the development of the microstructure of the hydrated products which control the evolution of the mechanical properties of the sample.

Taking into account Eq. 2, we assumed that at the very beginning of the hydration process the E values are proportional to the surface area of the sample.

In the time range from 0 to 4.5 h the E value increased, whereas in the subsequent time range the E value decreased, indicating the microstructure changes of the hydrated products. The decrease of the E values was due to the crystallization of the calcium silicate hydrated products.

Figure 2 depicts the experimental results of the ETA measurements of the water suspensions of $(\text{Ca}_3\text{SiO}_5)$ samples differing in surface area, namely 0.3 and $1.2 \text{ m}^2 \text{ g}^{-1}$, respectively. The $(\text{Ca}_3\text{SiO}_5)$ was mixed with water in the water/solid ratio $w/s = 0.4$.

It is obvious from Fig. 2 that the time dependence of the radon release rate, E , is affected by surface area values of the hydrating tricalcium-silicate sample. The differences in the microstructure development, namely the increase of surface area and the microstructure changes of the hydrating tricalcium-silicate samples were observed as dependent on the surface area values.

The time intervals where the microstructure changes during the tricalcium-silicate hydration were determined from the results of the ETA measurements (Fig. 2).

Figure 3 depicts the effect of temperature on the hydration of tricalcium-silicate characterized by the ETA method during the hydration at temperatures of 25 and 35 °C, respectively. The sample was prepared at the water/solid ratio, $w/s = 0.4$.

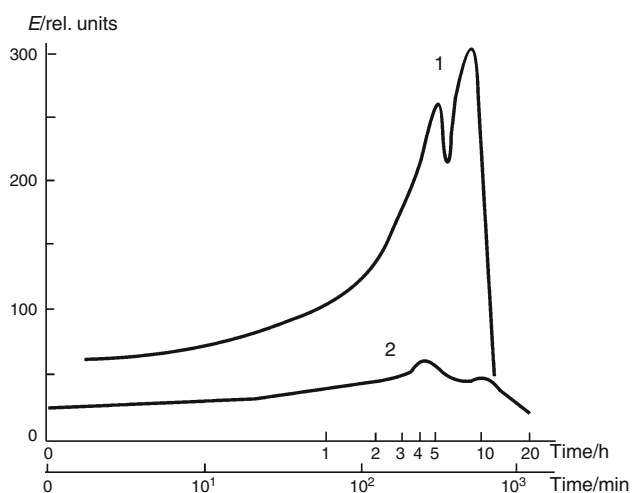


Fig. 2 Time dependence of radon release rate measured by ETA at the temperature of 25 °C during of hydration of the water suspensions of $(\text{Ca}_3\text{SiO}_5)$ samples differing in surface area, namely $1.2 \text{ m}^2 \text{ g}^{-1}$ (curve 1 sample B) and $0.3 \text{ m}^2 \text{ g}^{-1}$ (curve 2 sample A), respectively

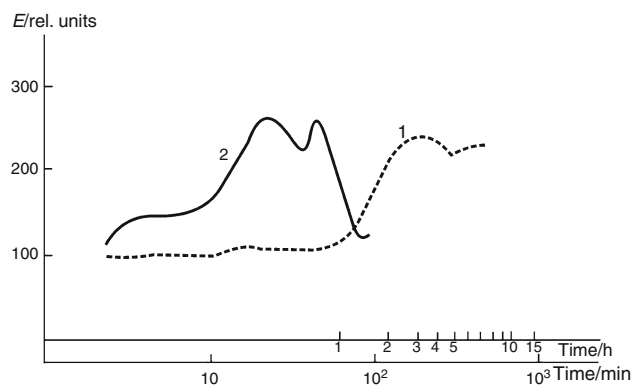


Fig. 3 Time dependence of radon release rate measured by ETA during hydration of $(\text{Ca}_3\text{SiO}_5)$, sample A, at the temperature of 25 °C (curve 1) and 35 °C (curve 2), respectively

The differences in the ETA results presented in Fig. 3 reflect the influence of the temperature on the hydration of the tricalcium-silicate sample. The induction period of hydration was considerably shortened for the hydration at the temperature of 35 °C in comparison with the hydration at the temperature of 25 °C.

Nevertheless, both of the ETA results measured at the hydration temperature of 25 and 35 °C, respectively, exhibited similar effects in the subsequent hydration stage, which confirmed the similarity of the structure of hydration products formed. The effects on the ETA curves characterized the microstructure changes of the hydration products.

Computer modeling of radon migration during tricalcium-silicate hydration

The mathematical model considered the formation of intermediate metastable hydration products, which are transformed into final hydration products.

It is supposed in the modeling that the formation and growth of amorphous hydration products takes place in the early hydration of $(\text{Ca}_3\text{SiO}_5)$. In the “three components model,” we have supposed [9] that the intermediate metastable phase is being formed on the surface of the grains of the initial phase.

Following parameters were used in the modeling radon release rate: L is the thickness of sample, E is the emanation rate (radon release 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, respectively. ($D_3 \gg D_1$ and $D_3 \gg D_2$).

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:

$$E(t) = E_1 + E_2 + E_3 \quad (3)$$

The emanation rate of the slab-like sample can be expressed by Eq. 4.

$$E_i = \frac{1}{L} \left(\frac{D_i}{\lambda} \right)^{1/2} \text{th}L \left(\frac{\lambda}{D_i} \right)^{1/2} \quad (4)$$

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, D , can be expressed by Eq. 5, considering Arrhenius law

$$D = D_0 \exp\left(-\frac{Q}{RT}\right) \quad (5)$$

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 in Kelvin.

The computer modeling enabled us to obtain time dependences of the concentrations of the initial, final, and intermediate phases, respectively. The amount of the initial phase monotonously decreased from 1 to 0, whereas the amount of the final phase increased from 0 to 1. The time dependence of the amount of the intermediate metastable phase 3 is described by a peak-like curve.

The “three components model” used [9] 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. In this way, it was demonstrated that 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.

Figure 4 depicts the model curves of the time dependence of the radon release rate of the hydration. A two-stage process of the microstructure development during the tricalcium-silicate hydration is reflected.

The curves presented in Fig. 4, correspond to the subsequent stages of the microstructure development characterizing the initial (curve 1) and final (curve 2) stage of the tricalcium-silicate hydration. The overall curve (curve 3) reflects the general view of the time dependence of the radon release rate during the tricalcium-silicate hydration.

From the comparison of the computer modeling results (Fig. 4) and experimental results obtained by ETA (Fig. 1), it followed that the model used in this article well characterized the microstructure development during tricalcium-silicate hydration. This model can be used in the

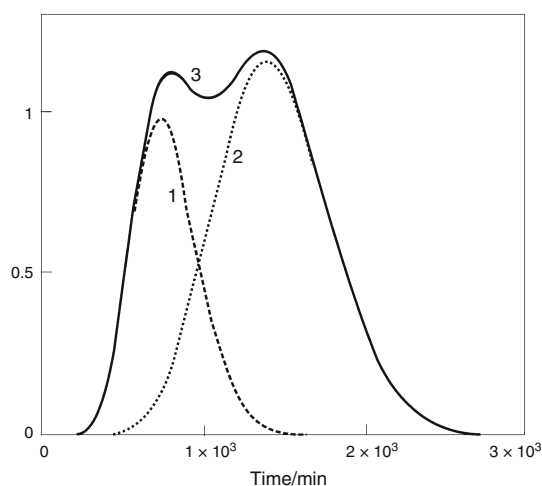


Fig. 4 Model curves of the time dependence of the radon release rate of the tricalcium-silicate hydration *curve 1* and *2* correspond to the subsequent stages of characterizing the initial and final stage of the hydration, *curve 3* corresponds to the summarized values of the radon release rate during the tricalcium-silicate hydration

evaluation of the experimental result of ETA to describe the microstructure development during the hydration of cement binders.

Conclusions

The ETA was used to characterize the microstructure development during hydration of tricalcium-silicate. Computer modeling results were in an agreement the experimental results the ETA making possible to characterize morphology changes during the hydration process. This technique can be advantageously applied also in the investigation of fixation of nuclear waste by cementation, where especially the conditions of the cement hydration are important.

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