THEORY OF EMANATION THERMAL ANALYSIS.
VI. MATHEMATICAL MODEL OF INERT GAS RELEASE
FROM A TWO-PHASE SOLID–FLUID SYSTEM
UNDER ITS INTERFACE AND DIFFUSIVITY CHANGES
DUE TO A CHEMICAL REACTION *

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ABSTRACT

A mathematical model of the release of inert gas from a two-phase system with changing solid-particle surfaces; the overall diffusivity changes of the system arising from chemical reaction are also given. The explicit form of the model is derived from the emanation rate from surface labeled calcium silicates during their hydration. Emanation curves under the assumption of the Pommersheim–Clifton model of hydration kinetics are simulated on a computer and good agreement with experimental results is demonstrated for the hydration of powdered tricalcium silicate.

INTRODUCTION

There are many cases in material science of systems of a powdered solid substance reacting with a liquid or a gas to form an agglomerated solid. The intermediary stages of such complex reaction processes include changes of the magnitude and quality of the reacting particles' surfaces as well as the area originally filled by the second reacting phase.

Emanation thermal analysis [1–3], which has been shown to give quantitative information about the structural changes of polymorphous materials [4–6], can serve as a powerful aid in such studies. Good agreement of the emanation rate curve with the kinetics of the hydration of calcium silicates,

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* Dedicated to Prof. W.W. Wendlandt on the occasion of this 60th birthday, in recognition of his contributions to the development of non-traditional methods of thermal analysis and acknowledging the promotion and steady interest he has given to emanation thermal analysis.

as well as more complex cement-based mixtures, has been shown both qualitatively [7–9] and semiquantitatively [10]. The purpose of this paper is to give a more detailed account of a generalized mathematical model and to verify its applicability to experimental results.

GENERAL THEORY

Basic assumptions and the general form of the model

Let us assume a solid material in the form of a collection of spherical grains whose radii are distributed according to some function $p(r_g)$, which are in contact with a reacting fluid phase filling all the space between the grains. The surfaces of the grains are impregnated by a relatively long-lived parent radionuclide such as ^{228}Th, which decays with the constant λ_T to an intermediary nuclide, such as ^{224}Ra, with a stationary concentration $c_R(r)$ on the radius r ($c_R(r) = 0$ for $r_g - r \geqslant \rho_R$ where ρ_R is the range of the nuclide); the intermediary nuclide decays, with constant λ_R, to an inert radioactive gas, such as ^{220}Rn, which is, in the case of compact solid grains and a low temperature, freed from the grain almost exclusively by recoil, after which it is transported by diffusion through the fluid phase in the pores and is measured on the surface of the sample.

The negligible concentration of the radionuclides in 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.

On the basis of the quasicontinuum–domain (QCD) model [11], we consider the porous space filled by the liquid or gaseous phase to be a diffusion quasicontinuum, the value of the main diffusion coefficient, $D(t)$, depending on the degree of the reaction and, thus, on time. We assume that the only free surface for the final transport of the measured gas 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; if we label the corresponding coordinate x ranging from zero on the surface and h on the bottom of the sample, the gas transport should be given by the relation between $\partial c/\partial t$ and $\partial^2 c/\partial x^2$. According to the methodology of the QCD model [11], we assume that the creation of the diffusant in the quasicontinuum by its emission from the grains can be approximated by a source function $\zeta(t)$ which depends exclusively on time. This assumption is based on the fact that the distances in the vicinity of the grain surface at which the function ζ can be spatially dependent to a significant extent are very small relative to the dimensions of the sample and comparable with the length of one diffusion jump so that, statistically, the spatial fluctuations of the ζ-value are leveled down almost instantaneously. Therefore, if the decay constant of the inert gas is λ, its concentration in the

quasicontinuum has to follow, approximately at least, the diffusion equation:

$$\frac{\partial c(x, t)}{\partial t} = D(t)\frac{\partial^2 c(x, t)}{\partial x^2} - \lambda c(x, t) + \zeta(t) \tag{1}$$

The explicit form of eqn. (1) depends, of course, on the expressions for $D(t)$ and $\zeta(t)$.

The source function $\zeta(t)$

If recoil is assumed to be the sole form of the gas transport from the grain, the source function is, to a good approximation, given by

$$\zeta(t) = v\int_{R_{min}}^{R_{max}} p(r_g)\left[\bar{e}_R(r_g, t) - \int_{R_{min}}^{R_{max}} p'(\rho, r_g)\xi(\rho, r_g)\,d\rho\right]dr_g \tag{2}$$

where R_{min} and R_{max} are the least and greatest values of r_g, respectively, v is the normalizing factor and $\bar{e}_R(r_g, t)$ is the recoil emanation rate from the grain with original radius r_g; $p'(\rho, r_g)$ is the probability of the grain with radius ρ to be in the vicinity of the grain and $\xi(\rho, r_g)$ is its trapping factor for the gas atoms emitted by recoil. Considering, however, the complications of the trapping phenomenon [5], we prefer to include a main correction for trapping directly into $\bar{e}_R(r_g, t)$ and to simplify eqn. (2) to

$$\zeta(t) = v\int_{R_{min}}^{R_{max}} p(r)\bar{e}_R(r, t)\,dr \tag{2a}$$

If the particles of the solid appear as more or less defined agglomerates of the elementary grain (assuming this to be of a uniform radius) so that $p(r)$ is a stepwise or, at least, a distinctly polymodal distribution, eqn. (2a) can be expressed as a sum

$$\zeta(t) = \sum_i p(r_i)\bar{e}_R(r_i, t) \tag{2b}$$

where $p(r_i)$ is the number fraction of the i-th agglomerate.

The explicit form of $\zeta(t)$ or $\bar{e}_R(r_g, t)$ is, however, rather complex in the case of the changing grain surface during the reaction. Usually, 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 given instant, are being transferred to the surface by the reaction and are thus available directly for the diffusion in the porous quasicontinuum. There should exist some critical degree of the overall reaction α_c, at which virtually all these atoms are, effectively, on the surface or decayed. In such a way, the ongoing reaction enhances the value of $\zeta(t)$, up to α_c at least. However, the space between the grains is filled progres-

sively by the newly formed material which can trap the gas atoms emitted by recoil and thus lower the effective value of $\zeta(t)$. The exact mathematical form of these two correction factors depends on the details of the process in question and thus cannot be given generally.

In a phenomenological approach to the problem the following expression for $\zeta(t)$ is proposed, reflecting both increasing and decreasing influence of $\alpha(t)$ on $\zeta(t)$:

$$\zeta(t) = \{\zeta_0 + (\zeta_m - \zeta_0)\exp[\delta_1(1 - \alpha_c/\alpha)]\}\exp(-\delta_2\alpha); \quad \alpha \in \langle 0, \alpha_c\rangle \quad (3a)$$

$$\zeta(t) = \zeta_m \exp(-\delta_2\alpha); \quad \alpha > \alpha_c \quad (3b)$$

where ζ_0 and ζ_m are the initial and maximum source (recoil) functions, respectively, i.e. (see refs. 4 and 5)

$$\zeta_0 = \frac{\pi}{2}r_g\lambda_T c_T\frac{\rho_r}{\rho_R}\left(r_g + \tfrac{1}{3}\rho_r\right) \quad (4a)$$

and

$$\zeta_m = 4\pi\lambda_T c_T r_g^2 \quad (4b)$$

here, r_g is the initial grain radius, c_T is the surface concentration of the parent nuclide and ρ_R, ρ_r are the respective ranges of the intermediary nuclide and the inert gas in the solid of the grain. In eqn. (3), δ_1 and δ_2 are empirical coefficients which have to be found for a given process and α_c is the critical value of the reaction degree α. The time dependence of the ζ value is thus a transformation of the time dependence of α which has to be established for the individual reaction process.

The diffusion coefficient D(t)

In the first approximation, we assume the diffusion of the inert gas through the solid reactant as well as through the solid reaction product to be negligible, relative to the diffusion through the quasicontinuum. If the relatively impermeable product adds to the surface of the solid grains and thus fills the space between the grains, the diffusion coefficient has to decrease progressively with the increasing reaction degree α. The form of the dependence proposed for $D(t)$ is given in eqn. (5):

$$D(t) = D(0)\exp(-\delta_3\alpha) + D(\infty) \quad (5)$$

where $D(0)$ corresponds to the initial Knudsen diffusion, i.e.

$$D(0) = 0.5r_g(8RT/3\pi M)^{0.5} \quad (5a)$$

(assuming the grains or agglomerates to be as small as to form a true porous space between them), and $D(\infty)$ is some final value, corresponding to the porosity of the product.

Emanation rate

According to our assumptions, the radioactive inert gas 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. The expression for the emanation rate must thus consist of two terms:

$$\bar{E}_R = N_p \left[\bar{e}_R(r_g)/3 - 0.25 r_g^2 3^{1/2} D(t) \frac{\partial c}{\partial x} \Big|_{x=0} \right] \tag{6}$$

where N_p is the number of surface grains. For the explicit form of eqn. (6), the solution of eqn. (1) has been shown [4] to be

$$c(x, t) = \bar{e}^{-\lambda t} \sum_{n=0}^{\infty} \cos[\beta_n(h-x)]\{b_n(t) + c_n(t)\} \tag{7}$$

where

$$b_n(t) = \frac{2}{h} \frac{\zeta(0)}{\lambda} \left\{ \frac{2h}{(2n+1)\pi} - \frac{1}{a^2 + \beta_n^2} \left[\beta_n - \frac{a}{\sinh(ah)} \right] \right\}$$

$$\times \exp\left[-\frac{n^2\pi^2}{h^2} \int_0^t D(\nu) \, d\nu \right] \tag{8}$$

and

$$c_n(t) = \frac{2}{h} \exp\left[-\frac{\pi^2 n^2}{h^2} \int_0^t D(\nu) \, d\nu \right] \int_0^t \zeta(s) \exp\left[\lambda s + \frac{\pi^2 n^2}{h^2} \int_0^t D(\nu) \, d\nu \right] ds \tag{9}$$

with

$$a = (\lambda/D(0))^{0.5}; \qquad \beta_n = (n + 0.5)\pi/h \tag{10}$$

According to this eqn. (6) can be rewritten in the form

$$\bar{E}_R = \frac{N_p r_g}{2} \left\{ \pi \lambda_T c_T \frac{\rho_r}{\rho_R} (r_g + \tfrac{1}{3}\rho_r) - r_g \frac{3^{1/2}}{2} D(t) \bar{e}^{-\lambda t} \sum_{n=0}^{\infty} \beta_n [b_n(t) + c_n(t)] \right\} \tag{11}$$

Equation (11), with eqns. (3), (5), (8), (9) and (10) is the master equation of the rate of emanation from a reacting sample. For the explicit form of eqn. (11) the dependence $\alpha(t)$ has to be found from an experimental study of the reaction kinetics.

SPECIFICATION, SIMULATION AND VERIFICATION OF THE MODEL

The specific form of the model for the hydration of calcium silicate, $3CaO \cdot SiO_2$ (C_3S)

The typical case for our model is that of calcium silicate, $3CaO \cdot SiO_2$, or more generally Portland cement mixtures reacting with water. According to the model proposed by Pommersheim and Clifton [12] for the hydration kinetics, the spherical grain of the silicate is supposed to react with water in a spherical zone proceeding from the outer surface of the grain to its center thus producing the voluminous outer layer of the secondary hydrate. Applying this model to the intact original silicate, the following differential equation can be deduced for the radius of the inner sphere

$$\frac{dr_i}{dt} = -\frac{r_g^3}{\tau r_i^2}\left[\left(\frac{D_i r_g}{Kr_i^2} + \frac{r_g}{r_i} - 1\right) + \frac{D_1}{D_x}\frac{x_0 \exp(-\beta_1 t)}{r_g} + \left(\frac{D_i}{D_o}\right)_0\right.$$

$$\left. \times \left[\frac{1}{\alpha_1 - (0.7 + \nu)(1 - r_i^3/r_g^3)}\right]^{1.5}\left\{1 - \left[1 + \nu(1 - r_i^3/r_g^3)\right]^{-1/3}\right\}\right]^{-1}$$

$$(12)$$

where $\alpha_1 = \gamma \cdot w/s$, γ being the specific weight and w/s the ratio of water to the original silicate; τ is the characteristic time, $\tau = a_1 r_g^2/c_0 D_i$, where a_1 is the number of water molecules needed for the hydration of one molecule of the silicate, c_0 is the concentration of the free ions of calcium or equivalent metal in the solution, D_1, D_o and D_x are the diffusion coefficients of water in the original silicate, in the secondary and in the primary hydrate, respectively, K is the rate constant of the primary hydration, x_0 is the thickness of the primary hydrate layer at the very start of the reaction and β is the rate constant of its disappearing. Equation (12) has to be solved by some numerical method, e.g. by some version of the Runge–Kutta procedure.

With the value of $r_i(t)$ at the current time, we define the reaction turnover α

$$\alpha(t) = 1 - \left(r_i(t)/r_g\right)^3 \tag{13}$$

by which the values of eqn. (11), via eqns. (3), (5), (8), (9) and (10) are obtainable.

Exploration of the model by its computer simulations

For the simulations of the emanation rate from hydrated calcium silicate (C_3S), the following initial values of the parameters have been used: $w/s =$
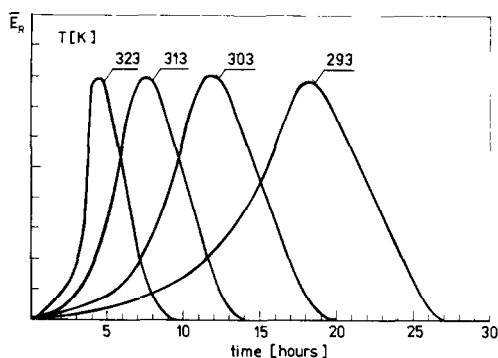
Fig. 1. Simulated curves of the emanation rate during hydration of $3CaO \cdot SiO_2$ at various temperatures (20–50 °C, i.e. 293–323 K); for other parameters see the text.

1.0, $a_1 = 1.0$, $\gamma = 3.2$, $\nu = 2.2$, $D_{i0} = 1.35 \times 10^{-5}$, $E_{D_i} = 40$ kJ mol^{-1}, $D_{x_0} = 0.82 \times 10^{-5}$, $E_{D_x} = 45$ kJ mol^{-1}, $D_{\infty} = 2.23 \times 10^{-5}$, $E_{D0} = 30$ kJ mol^{-1}, $x_0 = 3.5 \times 10^{-8}$ m, $\beta_0 = 0.6 \times 10^8$, $E_\beta = 40$ kJ mol^{-1}, $K_0 = 8.1$, $E_K = 40$ kJ mol, $r_g = 3.5 \times 10^{-6}$ m, $c_0 = 0.1$ mol l^{-1}, $T = 293$ K, $\delta_1 = 5.0$, $\delta_2 = 2.0$, $\delta_3 = 5.0$.

Some of these parameters were proposed by Pommersheim and Clifton [12], some were taken from our experiments. In the Figs. 1–9a the values of the emanation rate $\bar{E}_R$ are given in relative (non-dimensional) units, taking $\lambda_T c_T / \lambda_R = 1$. The experimental values of $\bar{E}_R$ in Fig. 9b are given in non-dimensional units obtained as the radon release rate of the sample, related to the radon release rate of the reference material.

Figure 1 shows the change of the simulated emanation rate curve with reaction temperature. In accordance with the experimental data, the maximum of the curves moves markedly to a shorter reaction time and its
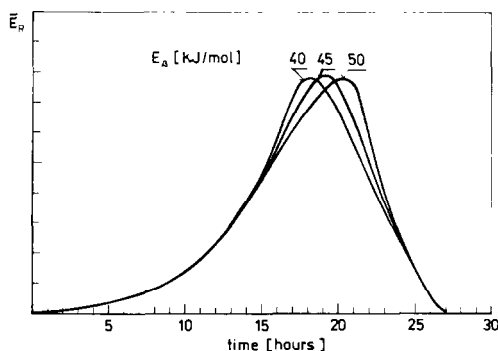

Fig. 2. Simulated curves of the emanation rate during hydration of $3CaO \cdot SiO_2$ at 293 K supposing various values of activation energies E_k of the primary hydration of the original calcium silicate; for other parameters see the text.
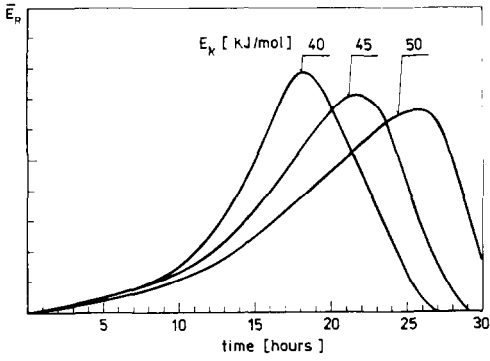
Fig. 3. Simulated curves of the emanation rate during hydration of $3CaO \cdot SiO_2$ at various values of activation energies E_{D_x} of the diffusion of water through the primary hydrate; for other parameters see the text.
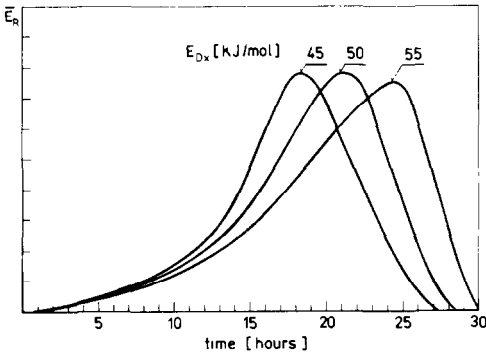

Fig. 4. Simulated curves of the emanation rate during hydration of $3CaO \cdot SiO_2$ at 293 K supposing various values of activation energies E of the disappearing of the primary hydrate, for other parameters see the text.
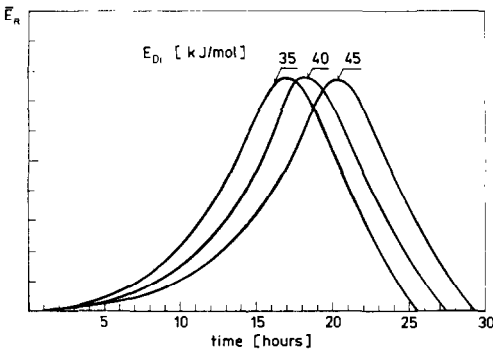

Fig. 5. Simulated curves of the emanation rate during hydration of $3CaO \cdot SiO_2$ at 293 K supposing various activation energies E_{D_i} of the diffusion of water through the intact calcium silicate; for other parameters see the text.
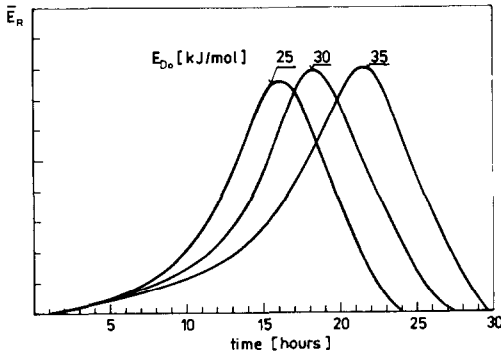
Fig. 6. Simulated curves of the emanation rate during hydration of $3CaO \cdot SiO_2$ at 293 K supposing various activation energies E_{D_0} of the diffusion of water through the secondary calcium silicate hydrate; for other parameters see the text.
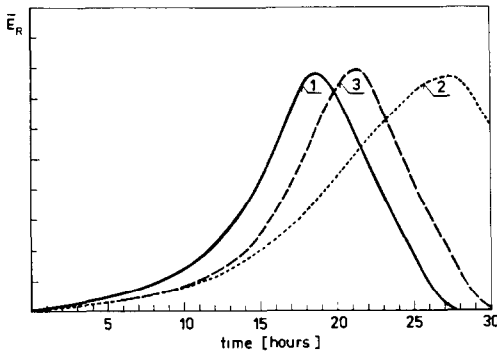

Fig. 7. Simulated curves of the emanation rate during hydration of $3CaO \cdot SiO_2$ at 293 K supposing various concentrations of Ca^{2+} (curve 2 corresponds to the concentration fivefold lower than the concentration represented by curve 1, curve 3 corresponds to the case of the increased concentration of Ca^{2+} due to the hydrolysis of calcium silicate; for detailed description see the text).
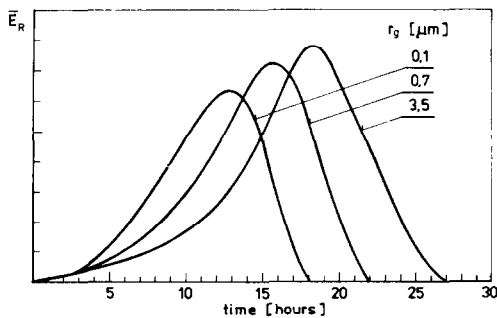

Fig. 8. Simulated curves of the emanation rate during hydration of $3CaO \cdot SiO_2$ supposing various grain size (0.1, 0.7 and 3.5 μm) at a temperature of 293 K.
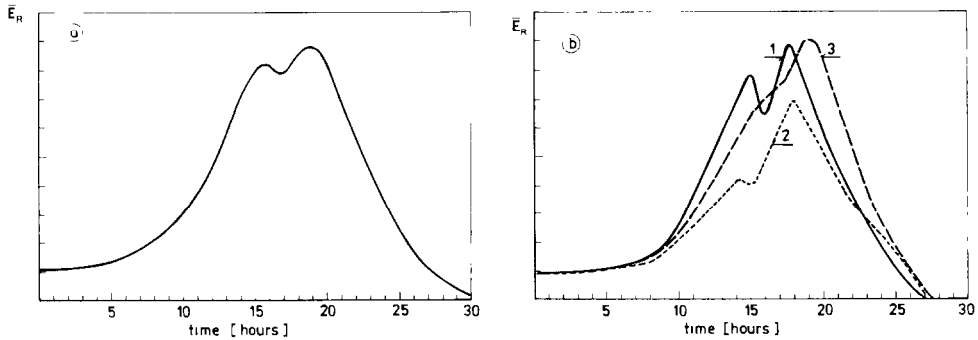
Fig. 9. Comparison of the simulated curve of emanation rate and experimental curves measured during hydration of $3CaO \cdot SiO_2$ at 293 K (W/solid = 0.4). (a) The simulated curve of emanation rate during hydration of a two-sized calcium silicate sample (grain sizes 0.7 and 3.5 μm). (b) Experimental curves of emanation rate of polydispersed samples of calcium silicate of various origin and surface area: (curve 1, surface area 1.2 m^2 g^{-1}; curve 2, surface area 0.3 m^2 g^{-1}; curve 3, the sample from which grains smaller than 0.5 μm were eliminated.)

half-width decreases at higher reaction temperature. To see which part of the model is the most sensitive to this, the individual activation energies of the elementary processes were changed with other parameters remaining constant; the results of these simulations are shown in Figs. 2 to 6. A comparison of the latter shows that the most pronounced influence is on the changes in E_K, E_{D_λ} and E_{D_0}, i.e. the activation energies of the net hydration reaction and of the water diffusion through the primary and the secondary hydrate, respectively. The further separation of these influences is rather difficult in theory as well as in physical reality.

Furthermore, the change of the theoretical curve caused by the change of c_0, i.e. the starting concentration of the polyvalent metal ion in the liquid phase, can be seen in Fig. 7; here, in the case of curve 2, this concentration has been decreased by a factor of 5, which brought about a marked change of the shape of the curve as well as a shift of its maximum to a longer reaction time.

If, however, the additional possibility of the gradual concentration increase by the primary silicate hydrolysis are included into the model by the equation

$$dc/dt = k_1\phi(1 - \alpha) - k_2 c \tag{14}$$

where k_1, k_2 are some reaction constants and ϕ is the stoichiometric factor, the shape of the curve and even the position of its maximum can be assimilated into the original one; this can be seen in curve 3 of Fig. 7. This supplement to the model reflects the case of the reaction suppression by some chelating agents and of its agitation by using the ion-rich solutions as the original liquid phase.

There is another parameter in the model which proves to be important in practical applications, viz. the radius of the original solid grain. In the

simulations shown so far, a uniform distribution of the grain size has been assumed. In a real sample, 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 is illustrated in Fig. 8 for the grain radii 0.1×10^{-6}, 0.7×10^{-6} and 3.5×10^{-6} m; the main change is, apparently, in the shift of the curve maximum to a shorter reaction time with the decreasing r_g.

Experimental verification of the model

In Fig. 9a the simulated curve of the emanation rate for hydration of a tricalcium silicate two-sized sample is shown. (The grain sizes $r_g = 0.7$ μm (50%) and $r_g = 3.5$ μm (50%) were assumed.) Comparing the three typical experimental curves of $3CaO \cdot SiO_2$ hydration in Fig. 9b (obtained from the hydration of three different samples of $3CaO \cdot SiO_2$) with Fig. 9a and simulated theoretical curves in Figs. 1 to 8, one can see a fairly good agreement between the experimental results and the model solutions. Taking into account that the history of the samples studied may strongly influence the kinetics of the tricalcium silicate hydration, the differences in the shapes of the curves in Fig. 9b may be ascribed to the different grain size and thermal treatment of the samples. Moreover, it can be supposed that two- or poly-sized tricalcium silicate samples can be characterized during their hydration by two or more more or less pronounced effects on the ETA curve measured at constant temperature. The ETA experimental results of Portland cement samples by Balek et al. [13] confirmed this supposition.

CONCLUSIONS

The mathematical model of radon release from solids under heterophase chemical reactions is given, taking into account the changes of the surface area and diffusion properties of the system under reaction. A general model is used to describe the experimental results of emanation thermal analysis during hydration of $3CaO \cdot SiO_2$ in isothermal conditions. The model solutions were compared with experimental curves of radon release rate from hydration samples, which differed in their history. On the bases of this model, the description of the behaviours of various samples of $3CaO \cdot SiO_2$ during hydration in different conditions can be made and the differences in the hydration can be evaluated.

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