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Radon atoms – a probe of the evolution of the hardened cement paste structure

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A new method of investigating the evolution of the hardened cement paste structure is proposed, based on the application of radon atoms as radioactive indicators. The application of this method (called the radiometric emanation method, REM) enabled us to follow continuously changes in the surface area and gel porosity directly during the setting and hardening of the cement paste, under conditions of required temperature and humidity. The advantage of the REM application in studying cement paste samples prepared of portland cement and slag cement (water to cement ratio = 0.3) at various temperatures from 20 up to 85° C is shown in comparison with commonly used methods.

1. Introduction

Methods applied to the investigation of cement hydration e.g. calorimetry, rheological measurement and measurements of electrical conductivity, specific surface area and porosity, give various views of the course of the cement hydration process. In this paper, the use of the radon atoms in the investigation of the evolution of the hardened cement paste structure during cement hydration is shown.

2. Principle of the application of radon atoms as radioactive indicators

Atoms of inert radioactive gases can be used as universal indicators of the physico-chemical state of solids and its changes [1]. They do not react with solids and are released from the solids during processes taking place in them.

As most investigated substances do not contain any radioactive gas, the measurement must be preceded by the incorporation of this gas into the samples (i.e. by the labelling of the samples). For this purpose, several ways were suggested [1]. The way most widely used for the labelling of samples by radon atoms is based on the incorporation of trace amounts of the parent radionuclides of radon into the substances investigated in the course of their preparation. The impregnation of the samples with a solution containing the parent radionuclides of radon can also be applied for this purpose. Radon atoms are formed as a result of spontaneous radioactive decay, e.g. according to the scheme

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

By using ^{228}Th and ^{224}Ra as parent radionuclides a practically permanent source of radon is incorporated into the investigated samples, which even makes it possible to perform time consuming experiments.

The term "radiometric emanation method" (REM) has been suggested by the present authors for the method based in measuring the rate of release of the radioactive gas from the sample. The radon release rate is expressed as the emanating power, defined as the ratio of the rate of the radon release to the rate of its formation in the labelled sample [1]. For the emanating power, E, of the porous solid the following relationship is valid

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

where S_{eff} is the effective surface area related to the mass of the sample, K_1 and K_2 are constants,

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D is the coefficient of the radon diffusion in the cement paste, λ is the decay constant of radon and ρ is the density of the sample.

The radiometric emanation method enables use to indicate changes of the inner surface area and the diffusion properties reflecting the evolution of the hardened cement paste samples. The detector of radioactivity used in the measurement of radon release from the sample ensures the high sensitivity of the method.

3. Experimental procedure

3.1. Preparation of the samples for the radiometric emanation method

The samples of the cement paste labelled with radon atoms were prepared by the impregnation of the cement (designated PC-400, from Lochkov, ČSSR, surface area $0.3\,m^2\,g^{-1}$) with acetone solution containing ^{228}Th and ^{224}Ra radioisotopes in the concentration of 10^5 Bq per 1 ml and by mixing the labelled cement with water in the ratio water to cement = 0.3. With regard to the safety rules, the labelling of cement and the preparation of the cement paste were made in a ventilated glove-box. The cement paste was homogenized by stirring (in the glove-box) and sampled. The mass of the sample used for one measurement was 1 g.

3.2. Measuring procedure of the radiometric emanation method

A schematic diagram of the apparatus for the radiometric emanation method is shown in Fig.1. The sample is held in the measuring cell at the required temperature and air is streamed through at a constant flow-rate which transports the radon atoms released into the detection chamber. The carrier gas, its humidity and chemical composition, can be chosen according to the requirements of the experiment; the carrier gas represents on one hand the medium in which the investigated process of the cement hydration proceeds, and on the other hand the carrier of the radon atoms released from the sample to the detection chamber. From the detection chamber the gas is carried out into the exhaust.

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 with a constant flow-rate of $0.87\,cm^3\,sec^{-1}$, which was saturated with water vapour to a relative humidity of $95 \pm 3\%$. The high relative humidity protected the sample from drying out during the measurement. The temperature of the sample was kept constant by means of a thermostat. For the detection of alpha radiation of radon a scintillation detector with a photomulitiplier was used in connection with an impulse counter provided with an output to the printer. The commercially produced apparatus for the radiometric emanation method by Netzsch Ltd, Selb, FRG) represents a part of a series of instruments for simultaneous thermal analysis [2].

The results of REM are presented as time dependence of the relative emanating power, 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 experiment, and A_{solid}

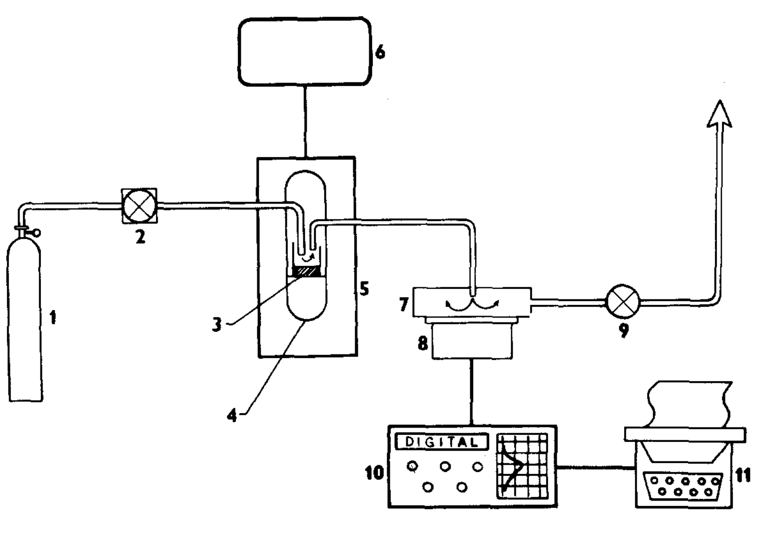

Figure 1 Scheme of the apparatus for the radiometric emanation method. 1, carrier gas supply; 2, stabilizer and flow-rate meter of the carrier gas; 3, the sample measured; 4, the measuring cell; 5, the thermostat; 6, the temperature controller of the measured sample; 7, the detection chamber of the radon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

is the total radioactivity of the sample, being proportional to the rate of radon formation in the sample.

3.3. Measuring procedures using common methods

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 [3].

Compressive strength, R_{ck}, was measured with cubes with an edge of 10 cm using the testing device made by Instron (USA). In the working range of 0 to 0.1 kN even very small strengths could be exactly registered.

The velocity of the propagation of ultrasonic waves, V_L, was determined by means of a Reco apparatus, type USG4 + UEM4 (G. D. R.) equipped with an transducer with a natural frequency of 46 kHz. The length of the measuring base was equal to 8 cm. A good transfer of the ultrasonic signal from the transducer to the sample was ensured by an efficient coupling agent.

The time dependence of the hydration reaction was investigated by means of conductivity calorimetry [4].

The standard Vicat test was used for checking the beginning and the end of the setting period of cement paste.

The scanning electron microscope by JEOL (Japan) was used for checking the evolution of the hardened cement paste structure at selected hydration times.

4. Results and discussion

As the radiometic solution method is used for the first time in the investigation of the evolution of a hardened cement paste structure, the results of this method are compared in this paper with those obtained by some currently used methods.

4.1. Comparison of the REM results with results of other methods

In the evolution of the structure of hardened cement paste several stages are usually distinguished:

(a) the period of initial hydration, occurring immediately after the mixing of cement with water, when only a few per cent of the total amount of clinker minerals react; the resulting hydration products form a layer on the surface of cement which stops the hydration reaction;

(b) the induction period, which is a result of the formation of the above mentioned layer of hydration products on the surface of the cement grains. The structure of the cement paste has a coagulated character and the rate of hydration reactions is low;

(c) the period of the destruction of the protecting layer formed by the hydration products, during which the rate of the hydration reaction substantially increases;

(d) the period of the gradual slowing down of the hydration reactions. In this period the hydration is limited by the diffusion of water through the layer of the hydration product.

The evolution of the structure of the hardened cement paste is controlled by a number of physicochemical processes, in the course of which the initial coagulation structure of the cement paste changes into the thermodynamically more stable structure of the cement stone. In this paper the curves obtained by the radiometric emanation method are analysed with regard to the stages of the hydration process mentioned above.

In Fig. 2 the REM curve (Curve 1) is compared with the calorimetric measurement (Curve 2) and with the measurement of the velocity of ultrasonic waves (Curve 3). The REM curve reflects clearly the above stages of the hydration process. After several minutes from mixing the cement with the water the relative emanating power, E, decreases. This decrease indicates the formation of hydration products on the surface of cement grains and the slowing down of the initial rate of hydration. In the following interval E remains practically constant. The destruction of the surface layer of the hydration products results in the intense increase of the relative emanating power after the end of the induction period. In this most intensive stage of hydration the amount of gelatineous hydration products rapidly increases; the specific surface area of these is several orders of magnitude higher than that of the original cement powder.

This stage of hydration, i.e. after the end of the induction period, can be described for example by the Avrami equation corresponding to the model of random nucleation of the product followed by the growth of crystallization nuclei. This equation describes the time dependence of the degree of transformation x, as follows

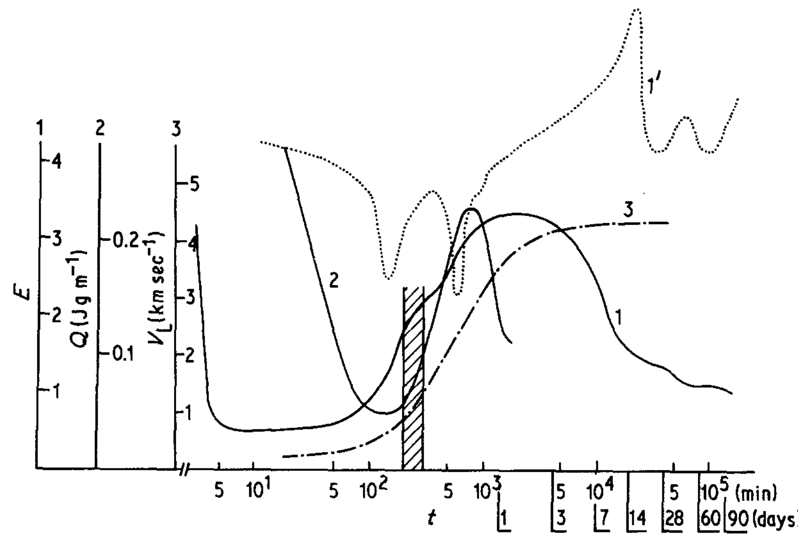

Figure 2 Comparison of time dependence of measured parameters characterizing the evolution of the hardened cement paste structure (Portland cement PC 400, at a temperature of 20° C: Curve 1, relative emanating power E; Curve 2, rate of the liberation of hydration heat, Q; Curve 3, impulse velocity of ultrasonic waves, V_L. The interval between the beginning and the end of setting of the cement paste determined by standard Vicat test is marked by hatching.

$$x = 1 - \exp(-kt^n) \quad (3)$$

The constant k depends on influences characterizing the rate of nucleation and of growth of the new formations. The constant n represents the reaction order. The course of the time dependence of the emanating power in the stage after the end of the incubation period is analgous to the time dependence of the first derivative of the degree of transformation. Therefore, the structural changes indicated in this hydration stage by the changes of emanating power, E, can be described by the Avrami equation.

The changes of the relative emanating power, E, (Curve 1) are shown more clearly by the curve of its first derivative (curve 1′). The peaks on the Curve 1′ indicate accurately the time intervals of the hydration stages mentioned above. The curve of the REM during the first 24 h of the hydration of cement reflects sensitively the evolution of the structure during setting and hardening of the cement paste.

The processes taking place during the cement hydration lead not only to an increase of the surface area of the sample but also to a change of porosity. This latter change causes the decrease of the relative emanating power of the sample although the surface area continues to increase. The decrease of E of the cement paste after 24 h from the start of the hydration (see Curve 1 in Fig. 2) can be ascribed to the recrystallization processes which influence the diffusion of radon in the porous sample; decrease of E indicates at the same time the compacting of the cement paste structure and the rise of the strength of the material tested (see the micrographs in Fig. 3).

The calorimetric curve (Fig. 2, Curve 2) characterizes the general course of the cement hydration reaction. However, the heat effect of the reaction does not consistently reflect the individual processes taking place during the cement hydration, as their thermal effects might mutually overlap. On the other hand, the radiometric emanation method gives information on individual processes causing the change of microstructure and of surface area regardless of their heat effects.

Curve 3 in Fig. 2 shows the time dependence of the impulse velocity, V_L, of the ultrasonic waves in the cement paste during hydration. The steep increase in this velocity indicates the structural changes of the cement paste. From a comparison of Curves 1 and 3 in Fig. 2 it follows that the method of ultrasonic waves and the radiometric emanation method reveal the kinetics of the microstructural changes during setting of the cement paste in a similar way, although they are based on different physical principles.

In Fig. 4 the time dependence of the REM curve (Curve 1) is compared with that of penetration resistance R_F (Curve 2) and compressive strength R_{ck} (Curve 3) of the cement paste specimens investigated. From Fig. 4 it is evident that the rise of the penetration resistance is closely connected to the increase of the relative emanating power E. The onset of the rise of penetration resistance fits well with the peak of the curve 1′, Fig. 4, which expresses the first derivative of E. The second peak of the curve 1′ fits with the onset of the mechanical resistance increase so that the values of the compressive strength become measurable (curve 3 in Fig. 4).

As can be seen from the results of the radiometric emanation method mentioned above, the theoretical model of the radon release from porous solids agress well with experiments. The changes in the relative emanating power 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, Cf. Equation 2).

For example, saturating a sample of hardened cement paste with water and subsequently drying it causes a change of the gel pores. When a sample of the hardened cement paste was stored in air of various humidities, the changes in its porosity were clearly indicated by the changes of the emanating power. Fig. 5 shows the dependence of the relative emanating power E of a sample of hardened cement paste (14 days of hydration) on the time of exposure to air with various water vapour pressures.

The results demonstrated in Fig. 5 at the same time confirm the views [5] supposing the reversibility of the changes of the space between layers of the dried C–S–H gel caused by the penetration of water molecules into the gel pores.

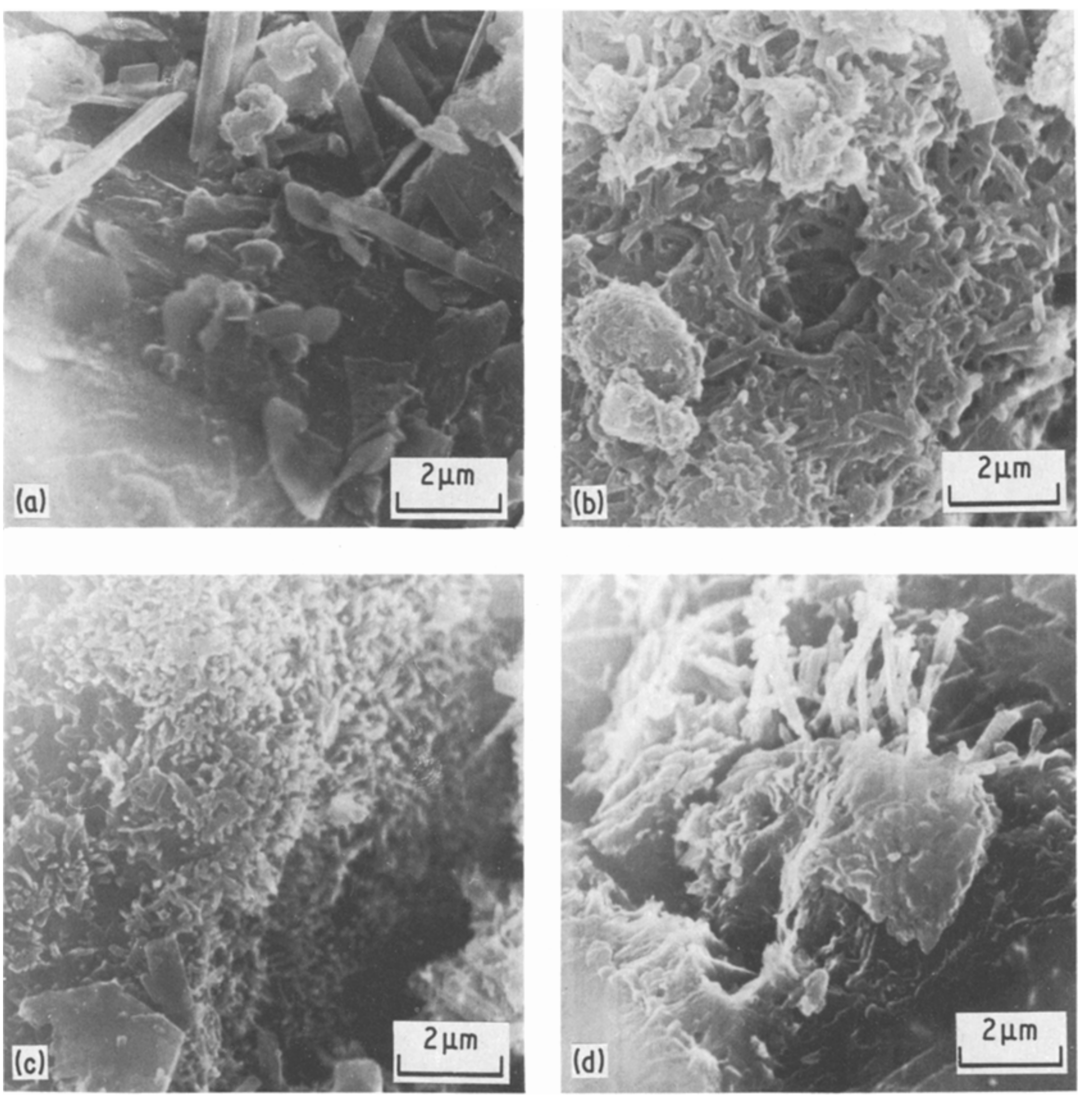

Figure 3 Scanning electron micrographs of cement paste samples (Portland cement PC 400) of the following hydration times: (a) 30 min, (b) 140 min, (c) 580 min and (d) 28 days (× 7800).

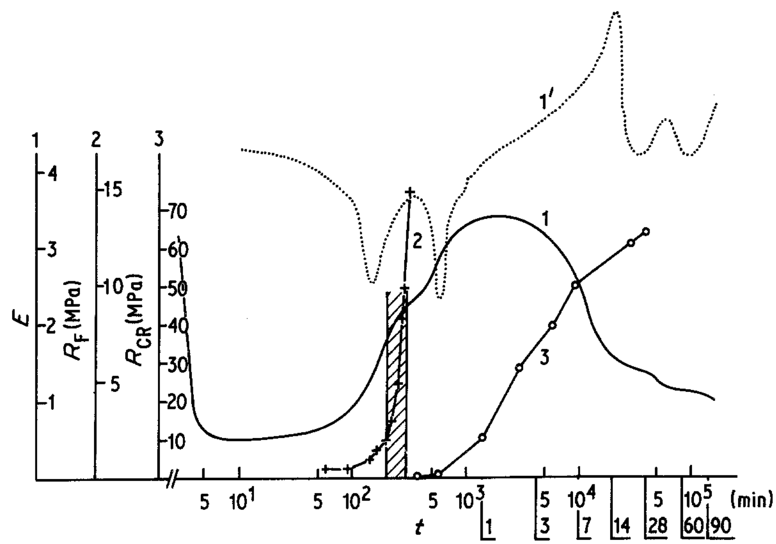

Figure 4 Comparison of time dependences of measured parameters characterizing the evolution of the hardened cement paste structure (Portland cement PC 400) at a temperature of 20° C: Curve 1, relative emanating power E; Curve 1', first derivative of E. Curve 2, the penetration resistance R_F; Curve 3, the compressive strength R_{ck}. The interval between the beginning and the end of setting of the cement paste determined by standard Vicat test is marked by hatching.

4.2. Cement hydration at elevated temperatures

It was shown in the preceding paragraphs that the radiometric emanation method can be advantageously used for the investigation of the hardened cement paste structure under various conditions. The apparatus gives the possibility of modelling the technological conditions of elevated temperature. Fig. 6 presents the REM curves obtained during the hydration of Portland cement obtained at temperatures of 35, 45 and 85° C. Simultaneously, the curves of time dependence of penetration resistance, R_F, of the cement paste samples measured at these temperatures are shown. The course of the REM curves in Fig. 6 reflects the known fact that the structure changes occurring during the cement paste setting are accelerated at elevated temperatures.

The influence of temperature on the rate of structure transformation taking place during the cement hydration is well described by the Arrhenius equation

$$k = Z\exp(-\omega/RT) \qquad (4)$$

where k is the rate constant from the Avrami equation (Equation 3), Z is the pre-exponential factor, ω is the quotient of the structure transformation indicated by the changes of the emanating power (formally representing the apparent activation energy of the transformation), R is the gas constant and T is the absolute temperature.

From the comparison of the curves shown in Fig. 6 it follows that the radiometric emanation method gives the possibility of indirectly characterizing changes in the physico-mechanical properties of the cement paste also at elevated tem-

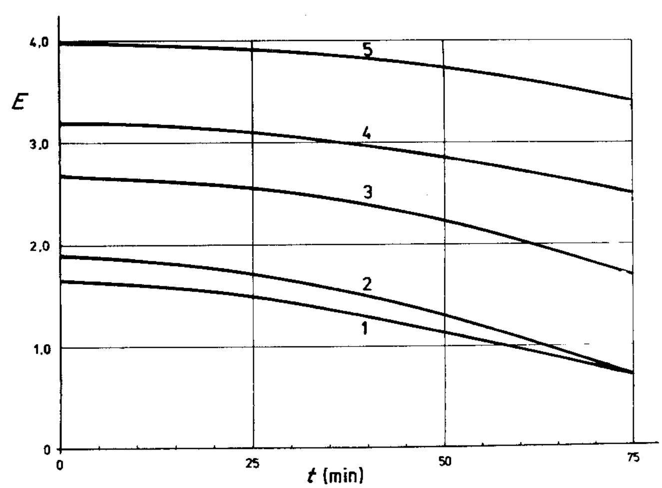

Figure 5 Relative emanating power, E, of a Portland cement paste sample aged 14 days, during its drying in air of 65 ± 3 % humidity. Between the measurements the sample was kept in air of 95 ± 3 % humidity. The curves correspond to the following time intervals of sample storage at the high humidity: Curve 1, 1 h 20 min; Curve 2, 3 h 15 min; Curve 3, 11 h 45 min. Curve 4, 17 h 15 min; and Curve 5, 22 h.

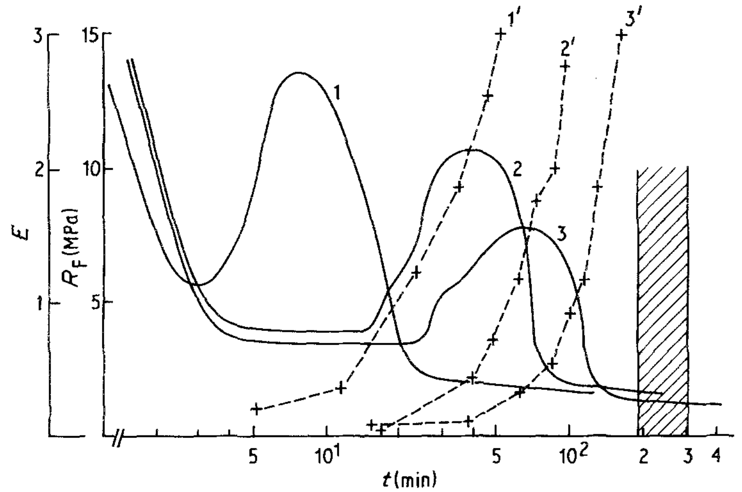

Figure 6 Time dependence of the relative emanating power E and the penetration resistance R_F characterizing the evolution of the hardened cement paste structure (Portland cement PC 400) at temperatures of 35° C (Curves 1 and 1'), 45° C (Curves 2 and 2') and 85° C (Curves 3 and 3'). The interval between the beginning and the end of the setting of the cement paste determined by standard Vicat test at 20° C is marked by hatching.

peratures. Moreover, 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.

In Fig. 6, a mutual shift of the corresponding curve of REM and penetration resistance measured at 45 and 85° C can be observed. This shift is caused by a systematic error resulting from the cooling of the samples when removed from the thermostat in order to perform a discontinuous measurement of the penetration resistance at room temperature.

The results obtained by the radiometric emanation method 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 the temperature influence on their hydration. Supposing that both the Avrami and the Arrhenius equations are valid, we may describe the reaction of the cement hydration after the end of the incubation period (i.e. in the time interval limited by the steep increase and the decrease of the relative emanating power E in Fig. 6) by Equation 5

$$dx/dt = Z \exp(-\omega/RT)(1-x)^n \qquad (5)$$

If the REM curves measured during the cement hydration at various temperatures (Curves 1, 2 and 3 in Fig. 6) are integrated in this interval, the degree of structure transformation x can be determined. From the x-values in time–dependence co-ordinates it is possible to calculate by multiple linear regression the values of the constants ω, Z and n. By means of the values of these constants it is possible to characterize the influence of temperatures on the cement paste setting process.

The parameters ω, Z and n characterize the dependence of the rate of cement paste setting on temperature, the induction period of this process and the reaction order, respectively. These parameters also characterize the temperature dependence of the changes of physico-mechanical properties of the hardened cement paste.

As an example, the parameters Z, ω and n determined from the REM curves measured during the hydration of two kinds of cement (Portland

TABLE I Cement hydration process characteristics

Cement sample	Temperature (° C)	n	ω (kJ mol^{-1})	ln Z
Portland cement (PC 400, Lochkov)	35	3.31	18.63	46.76
	45	3.07		
	65	2.64		
	85	2.39		
Slag cement (SPC 325, Čížkovice)	35	3.13	13.89	30.63
	45	3.28		
	65	3.38		
	85	2.78		

cement, PC 400, from Lochkov and slag cement, SPC 325, from Čižkovice, ČSSR) at temperatures of 35, 45, 65 and 85° C are presented in Table I.

The values of the parameter n lie in the interval from 2.30 to 2.65 which corresponds to the result of the investigation of the kinetics of cement hydration by the calorimetric method.

The higher value of ω signifies that the hydration reaction of the respective cement is less influenced by temperature. The higher value of Z indicates a relatively longer induction period of the hydration reaction.

The evaluation by REM of the two kinds of cement from the viewpoint of the temperature influence on their hydration agrees with the results of the penetration methods or results obtained by means of rheoviscosimeters.

For the evaluation of REM experimental data, another method, based on the Avrami and the Arrhenius equations can be used, as well as the one mentioned above. The characteristic points of the bottom of the decreasing REM-curves after the intensive structure transformation of the cement paste can be used for this purpose. The temperature dependence of the characteristic points serves for comparing the temperature dependence of the evolution of cement paste structure for various cement samples.

5. Conclusion

The measurement of the release of radon atoms has been shown as a sensitive probe of the evolution of the structure of the hardened cement paste. This method makes it possible to assess especially the early stages of the cement paste setting. The results obtained by the proposed method agree well with those obtained by calorimetry, measurement of the penetration resistance, ultrasonic wave propagation and compressive strength. The radiometric emanation method can supply valuable information about the cement hydration from the viewpoint of the evolution of the cement paste structure. This viewpoint represents a determining factor for the physico-mechanical properties of the hardened cement paste.

The method proposed possesses several methodical advantages in comparison with commonly used methods. Whereas by the calorimetry information about the hydration degree can be achieved which cannot always reflect the structure changes taking place during the hydration process, the radiometic emanation method indicates sensitively just these changes. For the characterization of the cement hydration products by the measurements of specific surface area or porosity, the samples are used in which the hydration was stopped e.g. by drying, evacuating of freezing. These procedures might substantially change the structure, the specific surface or the porosity of the samples. By means of the radiometric emanation method, the evolution of the hardened cement paste structure can be followed continuously and directly under the conditions of required temperature and humidity. The results of this method supplement conveniently the data obtained by the common methods. The REM can be applied to the investigation of the hydration of cement binders also in practice, e.g. in the operative checking of the suitability of various cements used in the technology of the heat treated concrete.

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