ON HOW THE MOISTURE DIFFUSIVITY IN HYDRAULIC CEMENT IS AFFECTED BY THE TYPE OF BOND BETWEEN THE MOISTURE AND THE MATERIAL

V. G. Kamenskii and V. P. Zhuravleva

UDC 532.72

The moisture diffusivity a_m in hydraulic cement is calculated over the entire range of moisture content levels, including the wet and the hygroscopic state. The values obtained here account for the variation of the diffusivity as a function of the temperature and of the moisture content simultaneously.

A method of heat treating a mass of concrete with an electromagnetic field has been developed at the Institute of Heat and Mass Transfer (Academy of Sciences of the Belorussian SSR) and is now used in the industry [1, 2, 3]. It would be of interest to explore how this mode of heat treatment affects the structuromechanical properties of concrete.

The authors have calculated the moisture diffusivity in hydraulic cement (concrete) cured with an electromagnetic field at industrial frequency or (for comparison) in a hot-vapor chamber as well as under normal-humidity conditions. The calculations were based on the theory of heat and mass transfer during dehydration of a material [4]. Dehydration thermograms and curves [5] were used for determining this moisture diffusivity.

First we determined a_m during the period of constant-rate dehydration and used for this the formula [6]

$$a_m = \frac{0.266NR^2(\bar{u}_0 - 2.25u_e)}{(\bar{u}_0 - \bar{u})[\bar{u}_0 - 1.8(u_{mh} - u_e)]}. \tag{1}$$

Formula (1) had been derived by transforming the solution to the equation of mass transfer for an infinitely large plate with a low value of the Posnov number. The latter condition is quite well satisfied in any capillary-porous material during the period of constant-rate dehydration, when the internal temperature drop is either equal to zero or is negligibly small.

This period also corresponds to the linear horizontal segment of a dehydration thermogram. With the relation $a_m(\bar{u})$ between the moisture diffusivity and the moisture content at a constant temperature already known, it is possible to determine the fictitious moisture diffusivity a_0 in a bone-dry material. For this purpose here, we plotted a graph of $1/a_m$ vs $\bar{u}$. The resulting straight line was then extended to its intersection with the axis of ordinates. The intercept on this axis determined $1/a_0$ and thus also a_0.

The temperature characteristic of the fictitious moisture diffusivity a_0 in a bone-dry material can, for capillary-porous and colloidal materials, be expressed as follows [7]:

$$a_0 = a_{00}\cdot 10^5 \left(\frac{T}{1000}\right)^{20}, \tag{2}$$

$$a_0 = a_{00} \left(\frac{T}{1000}\right)^{10}. \tag{3}$$

Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 25, No. 4, pp. 694-700, October, 1973. Original article submitted April 4, 1973.

TABLE 1. Constants in the Formulas Relating the Moisture Diffusivity to the Moisture Content and to the Temperature, for Hydraulic Cement Cured by Various Methods of Heat Treatment

Method of heat treatment	T_M	$a_0\cdot 10^6$	a_{00}	k
N	335	0,91	0,0288	4,67
E	335	0,84	0,0266	5
V	335	1,48	0,0468	5,55

Note: N denotes normal-humidity cure; E denotes heat treatment with an electromagnetic field; V denotes hot-vapor treatment.

The coefficient a_{00} is independent of the temperature but depends on the properties of the material, and for hydraulic cement (a typical capillary-porous material) is calculated according to formula (2). The applicability of formula (2) to hydraulic cement has been demonstrated in [12], where data on the moisture diffusivity in hydraulic cement were approximated by this formula with sufficient accuracy for engineering calculations.

The relative moisture diffusivity in capillary-porous and colloidal materials can be related to the moisture content at a constant temperature according to the expression

$$\frac{a_0}{a_m} = 1 - k\bar{u}. \tag{4}$$

The coefficient k, constant for any given temperature, is found as the slope of the straight line which represents Eq. (4). The values of a_{00} and k found accordingly for hydraulic cement (concrete) cured by various methods are listed in Table 1.

It appears in this table that the values of a_{00} and k change, depending on the method by which concrete is cured. These values yielded the moisture diffusivity a_m during the period of decreasing-rate dehydration, on the basis of appropriate thermograms and curves with the temperature T and the moisture content $\bar{u}$ held constant through definite time intervals. Then the value of a_0 corresponding to a given temperature in the given mode of heat treatment was calculated according to formula (2). Finally, by inserting these values of a_0, $\bar{u}$, and k into (4), the moisture diffusivity a_m was obtained for any given instant of time during the dehydration process.

The moisture diffusivity a_m in hydraulic cement (concrete) cured by various methods is shown in Fig. 1, indicating that its value during electromagnetic heat treatment (I) is lower than during hot-vapor treatment (II) over the entire range of moisture content levels, and is lower than during normal-humidity cure (III) through the decreasing-rate period. This again confirms the conclusion that heat treatment with an electromagnetic field yields a more compact structure in hydraulic cement, where migration of moisture is more inhibited than in hot-vapor treated or even in normal-humidity cured material.

A comparison between the curves in Fig. 1 and the dehydration thermograms plotted in [5] for the 120°C temperature indicates the existence of critical points in both cases. Moreover, these points on the $a_m(\bar{u})$ curves coincide with those corresponding, in terms of dehydration time and moisture content, on the dehydration thermograms. This further confirms the validity of the empirical formulas used for calculations. It follows, therefore, that the critical points on our $a_m(\bar{u})$ curves as well as on Kazanskii's thermograms [8] represent transitions between different states of the moisture and its different types of bond with the material during the dehydration process. Thus, the segment between points 1 and 2 on the $t(\tau)$ thermogram and thus also on the $a_m(\bar{u})$ curve corresponds to capillary moisture, the segment between points 2 and 3 on the diagrams corresponds to adhesion in macropores, and the difference in moisture content levels between points 3 and 4 corresponds to capillary condensation in micropores. These three states of the moisture are, according to Kazanskii's schematic, associated with a physicomechanical bond between it and the material. Point 4 corresponds to the maximum content of polymolecular adsorption moisture, and point 5 corresponds to the maximum content of monomolecular adsorption moisture (with a physicochemical bond to the material).

For hydraulic cement heat treated with an electromagnetic field, also for hydraulic cement cured under normal-humidity conditions, there are six such critical points on the $a_m(\bar{u})$ curves. For hot-vapor treated hydraulic cement there are only five such points. There is no point 6 there which corresponds to

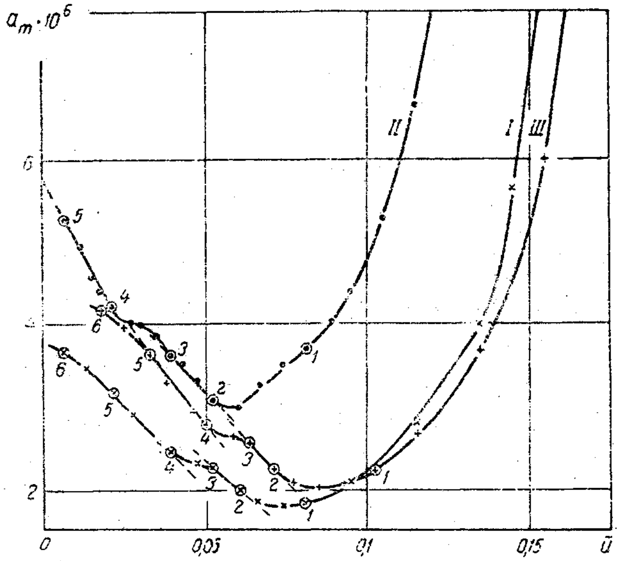

Fig. 1. Moisture diffusivity a_m (m^2/h) as a function of the moisture content $\bar{u}$ (kg/kg) in hydraulic cement (concrete) during heat treatment: I) with an electromagnetic field; II) with hot vapor; III) under normal-humidity conditions.

the maximum content of moisture with a weak chemical bond. This can be explained by a higher degree of cement hydration during heat treatment with an electromagnetic field than during conventional hot-vapor treatment.

It is also evident in Fig. 1 that, as soon as the adhesion moisture in macropores has been removed from the hydraulic cement (concrete) (point 2), the moisture diffusivity increases with decreasing moisture content. This can, apparently, be explained by a rise in the temperature of the material during this period of dehydration, which in turn leads to an increase in the diffusivity a_m.

One may conclude, finally, that heat treatment with an electromagnetic field enhances the porous structure of hydraulic cement by increasing the volume of micropores ($r < 10^{-5}$ cm) more than does hot-vapor treatment or normal-humidity cure. This again confirms the thesis in [5, 9] that the porous structure of hydraulic cement, its capability of retaining water by various types of bond, and, consequently, also the overall quality of the concrete are affected by the method of heat treatment during cure.

Before determining the moisture diffusivity a_m in hydraulic cement, a complex capillary-porous material in terms of both its porosity structure and its water retention characteristics, we have determined the moisture diffusivity in simpler materials (coarse-grain quartz sand, Chasov-Yarsk clay, Poltava clay, and cellulose). For this we use dehydration thermograms and kinetics curves which Kazanskii had obtained for those materials [10, 11]. For quartz sand, a representative capillary-porous material, as well as for hydraulic cement we calculated the moisture diffusivity in both periods of constant-rate and decreasing-rate dehydration, according to formulas (1) and (2), respectively. This moisture diffusivity, as a function of the moisture content and the temperature, is shown in Fig. 2 for quartz sand. The numbers 2 and 3 refer to points on the $a_m(\bar{u})$ curve which correspond, in terms of moisture content and dehydration time, to the critical points on the thermograms. According to Kazanskii's schematic, point 2 corresponds to the transition of moisture from capillary to adhesion state during evaporation in macropores of the body, and point 3 corresponds to the maximum hygroscopic moisture content. We note that in this case points 2 and 3 on the $a_m(\bar{u})$ curve are not very pronounced, just noticeable. On curve I they are more pronounced than on curve II. Point 2 on curve I represents the transition from decreasing to increasing moisture diffusivity, on curve II it represents the transition from sharply decreasing to slightly decreasing moisture diffusivity with decreasing moisture content. This is so, presumably, because curve I corresponds to a higher dehydration temperature ($t_d = 79$°C) than curve II ($t_d = 41$°C).

A reduced moisture content in the material during dehydration results in a reduced moisture diffusivity. Raising the temperature of the drying material to the ambient level, on the other hand, results in a higher moisture diffusivity. At relatively high dehydration temperatures, thus, the temperature becomes

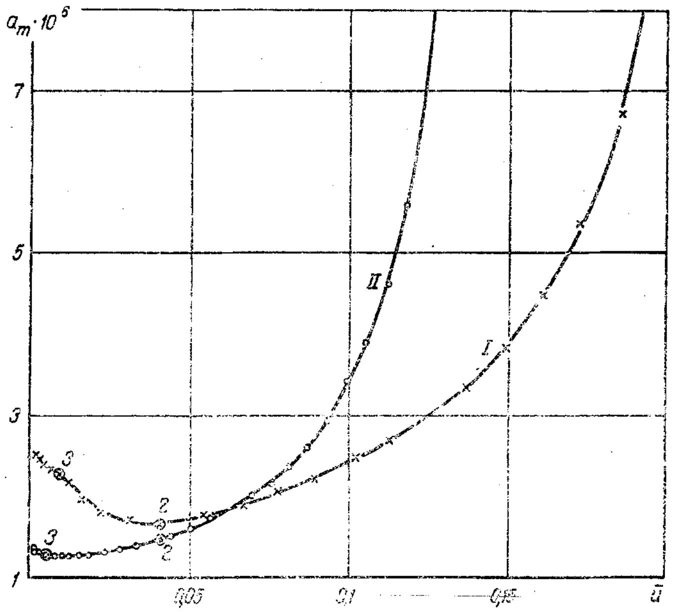

Fig. 2. Moisture diffusivity a_m (m^2/h) as a function of the moisture content $\bar{u}$ (kg/kg), in coarse-grain quartz sand at an ambient temperature: I) t_d = 79°C; II) 41.

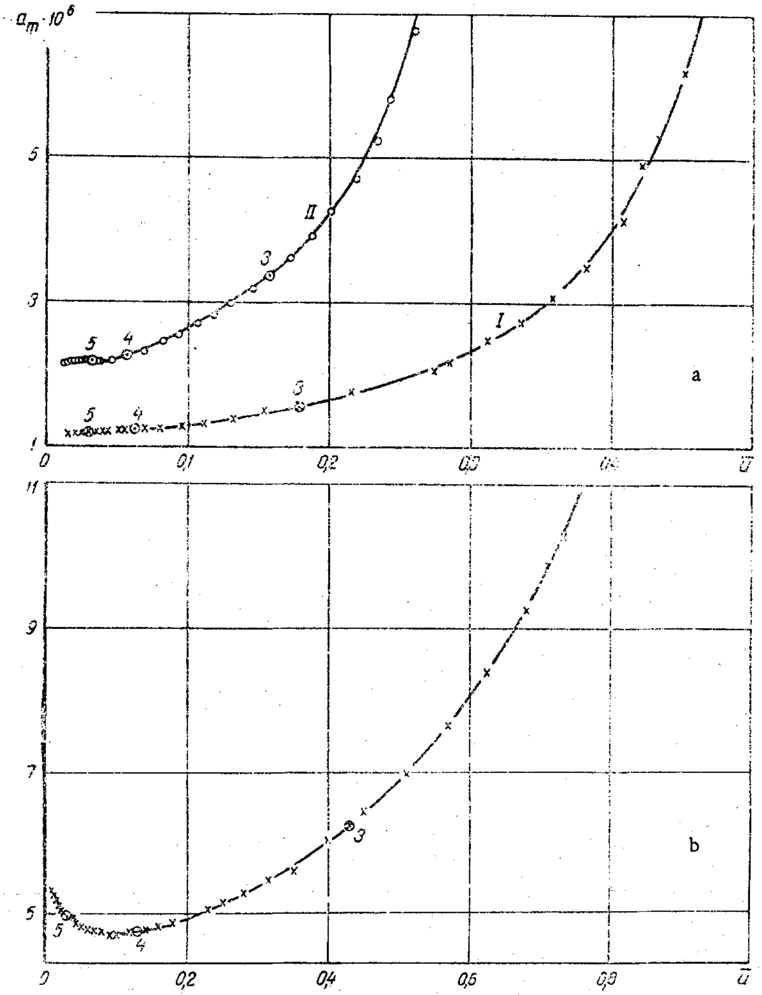

Fig. 3. Moisture diffusivity a_m (m^2/h) as a function of the moisture content $\bar{u}$ (kg/kg): a) Chasov-Yarsk clay (I) at t_d = 42°C and Poltava clay (II) at t_d = 60°C; b) cellulose at t_d = 35°C.

the dominant factor affecting the variation of a_m during the decreasing-rate period of dehydration. Inasmuch as the thermograms depicting the temperature variation during the dehydration process contain critical points, these are also reflected, to some extent (depending on the temperature) on our $a_m(\bar{u})$ curves.

The moisture diffusivity in Chasov-Yarsk and Poltava clays as well as in cellulose, all representative colloidal materials, was calculated according to formula (3). This formula had been obtained following an evaluation of very many data on the moisture diffusivity in colloidal materials and, especially, various clays [7]. On this basis, we could accept it as suitable for our calculations in this study.

The moisture diffusivity as a function of the moisture content is shown in Fig. 3a for Chasov-Yarsk and Poltava clays, in Fig. 4b for cellulose. The numbers 3, 4, and 5 refer to points on the $a_m(\bar{u})$ curves which coincide, in terms of moisture content, with the corresponding critical points on the dehydration thermograms. Hence, it may be assumed that, as on the dehydration thermograms, up to point 3 removed of the moisture of osmotic swelling occurs. The segment between points 3 and 4 corresponds to capillary moisture in micropores. There are no macropores in clay and in cellulose. The maximum content of polylayer adsorption moisture corresponds to point 4, that of monolayer adsorption moisture corresponds to point 5. We note that it would have been difficult in this case to indicate the critical points on the $a_m(\bar{u})$ curves without knowing, from the dehydration thermograms, the type of moisture bond in these materials.

With the aid of Kazanskii's dehydration thermograms and curves for several materials, it was thus possible to calculate the moisture diffusivity in those materials, as a function of both the moisture content and the temperature, under normal process conditions. It has been noted that, during dehydration at a relatively high temperature, the moisture diffusivity a_m depends more strongly on the temperature than on the moisture content. In this case there may appear critical points on the $a_m(\bar{u})$ curves which correspond to transitions from one type to another type of bond between the moisture and the material.

NOTATION

N	is the constant dehydration rate;
R	is the characteristic dimension of the specimen;
$\bar{u}_0$	is the initial moisture content;
$\bar{u}$	is the instantaneous moisture content;
u_{mh}	is the maximum hygroscopic moisture content;
u_e	is the equilibrium moisture content;
a_m	is the moisture diffusivity;
T	is the temperature;
τ	is the time.

LITERATURE CITED

1. A. V. Lykov and S. G. Romanovskii, Izv. Akad. Nauk BSSR, Ser. Fiz.-Tekh. Nauk, No. 2 (1966).
2. B. M. Smol'skii, in: Heat and Mass Transfer in Capillary-Porous Bodies [in Russian], Nauka i Tekhnika, Minsk (1965).
3. V. G. Kamenskii, G. Ya. Dan'ko, A. I. Li, and A. T. Selishchev, Prom. Belorussii, No. 12 (1970).
4. A. V. Lykov, Theory of Desiccation [in Russian], Énergiya, Moscow (1968).
5. L. Ya. Volosyan and V. M. Kazanskii, Inzh.-Fiz. Zh., 15, No. 5 (1968).
6. N. E. Gorobtsova, Inzh.-Fiz. Zh., 15, No. 2 (1968).
7. A. V. Lykov and V. P. Zhuravleva, in: Heat and Mass Transfer [in Russian], Vol. 6, Naukova Dumka, Kiev (1968).
8. M. F. Kazanskii, Dokl. Akad. Nauk SSSR, 130, No. 5 (1960).
9. L. Ya. Volosyan, V. P. Zhuravleva, and I. S. Yurkevich, Inzh.-Fiz. Zh., 21, No. 3 (1971).
10. M. F. Kazanskii, Doctor's Dissertation [in Russian], Minsk (1958).
11. M. F. Kazanskii, P. P. Lutsik, and V. N. Oleinikov, Proceedings of the Conference on Heat and Mass Transfer [in Russian], ITMO Akad. Nauk BSSR, Minsk (1961).
12. V. P. Zhuravleva, Mass and Heat Transfer during Heat Treatment and Dehydration of Capillary-Porous Structural Materials [in Russian], Nauka i Tekhnika, Minsk (1972).