THE USE OF DRYING THERMOGRAMS AND ENERGOGRAMS TO DETERMINE THE MOISTURE IN A WEAK CHEMICAL BOND WITH DISPERSE BODIES

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A combined analysis of drying thermograms and energograms for various disperse bodies demonstrates the possibility of using the method of drying thermograms to determine the quantity of moisture in weak chemical bond with a disperse body. An energy-based scheme is proposed for the successive removal of moisture in various forms of bonding by means of drying, including moisture that is chemically bound.

The method of drying thermograms [1] is used extensively to study the differential water-retaining properties of disperse bodies with respect to the forms and types of bonds for moisture retained by capillary and adsorption forces. The classification of disperse porous bodies includes the general group of cement stones and concretes of various compositions used widely throughout the national economy. An outstanding feature of the cement stones is the fact that within the moisture weakly bound to such stones we find that portion of the moisture in chemical bond that is retained by relatively weak chemical forces. The evaporation of this moisture from concretes takes place at temperatures of 310-330°K [2-4], which is close to the evaporation temperature of capillary and adsorbed moisture from these same bodies. Because of the weak bond, this moisture participates in the heat- and mass-transfer processes involved in the industrial processing of materials, even at comparatively low temperatures, and it significantly affects a number of the properties of the concrete. The determination of the differential water-retaining properties of such disperse bodies with consideration of the moisture not only in mechanical and physicochemical bond, but of the moisture in weak chemical bond, therefore involves a certain scientific and practical interest.

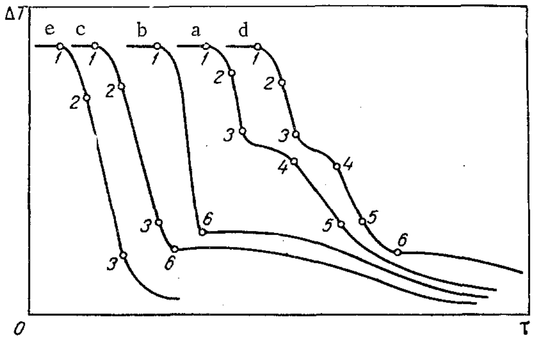

Fig. 1. Drying thermograms for MSM silica gel (a), calcium hydrosulfoaluminate (b), gypseous aluminous cement stone (c), a mixture of silica gel with calcium hydrosulfoaluminate (d), and quartz sand (e); [ΔT) temperature difference between the specimen and the air; τ) test duration].

Unfortunately, the method of drying thermograms – presently the only method for the simultaneous determination of the differential water-retaining properties of a body with respect to the various forms and kinds of moisture bond – has been developed exclusively for the investigation of the various forms of capillary and adsorbed moisture. It therefore becomes necessary to undertake a further study of the drying thermogram method to apply it as well to the determination of the moisture in weak chemical bond with a body. It is to the examination of these questions that this paper is devoted.

The method was developed through a joint analysis of the thermograms and energograms for the drying of cement-stone specimens containing moisture in weak chemical bond, and for specially prepared model capillary-porous bodies whose composition contained certain cement-stone components capable, on drying, of giving up the moisture in weak chemical bond. The drying thermograms in this case made it possible to determine the sequence for

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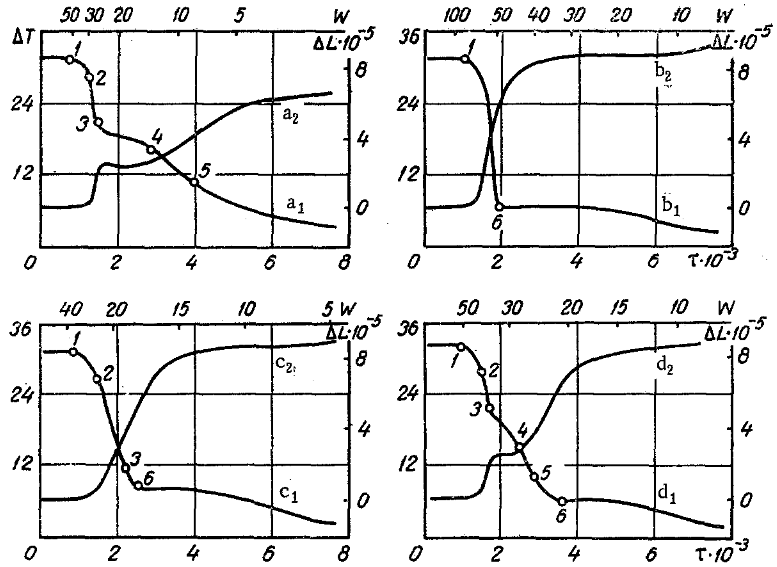

Fig. 2. Thermograms (curves a_1-d_1) and energograms (curves a_2-d_2) for MSM silica gel (a), for calcium hydrosulfoaluminate (b), for gypseous aluminous cement stone (c), and for a mixture of silica gel with the hydrosulfoaluminate (d); [ΔT) temperature difference between the specimen and the air, °C; ΔL) intrinsic moisture-binding energy, J/kg; τ) test duration, sec; W) moisture content, %].

the removal of the various forms and kinds of bonds linking the moisture to the body, and with the energograms we were able to determine the energy binding the moisture to the body.

We chose the following specimens for our study.

We selected MSM silica gel as a typical capillary-porous body capable of retaining substantial quantities of both capillary moisture in macro- and micropores, i.e., moisture in physicomechanical bond, as well as adsorbed moisture in one or more layers, i.e., moisture in physicochemical bond [5]. The water-retaining and structural properties of the MSM silica gel have been adequately studied [1, 6, 7]. A typical coarse-grained porous body capable of retaining moisture exclusively in macropores with radii in excess of 10^{-7} m was the quartz sand used in this study. We know that the quantity of adsorbed moisture in the quartz sands is negligibly small and does not exceed 0.1-0.2% [8].

As the typical substance containing easily released moisture in chemical bond we took calcium hydrosulfoaluminate $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$. This substance is completely stable at room temperature; however, with a rise in temperature it easily gives up a substantial portion of its structural water. Thus, at a temperature of 333°K the content of structural water is reduced to 12 molecules, while at a temperature of 393°K and at atmospheric pressure the structural water content drops to 8 molecules [2]. For the purposes of our investigation calcium hydrosulfoaluminate is particularly convenient because of its excellent reproducibility (a cp substance), as well as because of the fact that the quantity of adsorbed moisture and the moisture of the microcapillaries within it is extremely small. The calcium hydrosulfoaluminate was also chosen for the fact that it is included as one of the components in the cement stones which we selected for the study.

Mixing the calcium hydrosulfoaluminate in specific ratios with the quartz sand or with an MSM silica gel sand, we can produce model disperse bodies capable of retaining various and well-established quantities of moisture in weak chemical bond, as well as capillary and adsorbed moisture. A mixture of equal weights (based on the dry weight at 378°K) of MSM, silica gel, and the hydrosulfoaluminate was taken as such a model body in this study.

As an example of a real disperse body containing moisture in weak chemical bond – a material used extensively in practice – we chose a gypseous aluminous expanding cement stone which had been left standing for a year to stabilize its properties.

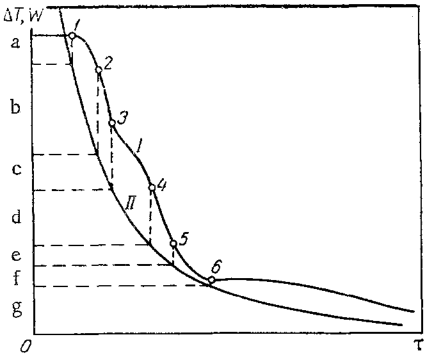

Fig. 3. Diagram showing the sequence for the removal, through drying, of moisture in various bond forms from a disperse body [I) thermogram; II) drying curve; ΔT) temperature difference between the specimen and the air; W) moisture content; τ) time]. The moisture-content segments along the axis of ordinates correspond to: a) excess free water above the body; b) moisture in the capillary state in the pores; c) the moisture at the ends of the macropores; d) capillary moisture of the micropores; e) moisture of polymolecular adsorption; f) moisture of monomolecular adsorption; g) moisture in weak chemical bond.

The drying thermograms for all of the specimens were recorded under isothermal conditions in the installation described in reference [9]. The calcium hydrosulfoaluminate was used in the form of a fine crystalline powder. All of the remaining specimens were used in the form of sand with grain dimensions of 0.25-0.50 mm. Thin layers (1-2 mm) of each of the experiments were moistened prior to the experiment in the cuvette of the installation, with a certain amount of excess free water above the surface. The thermograms recorded at 360°K and at an air pressure of about $4 \cdot 10^4$ N/m^2 in the heat and pressure chamber of the installation are shown in Fig. 1. The thermograms of these specimens were also taken at other temperatures (from 320 to 390°K) and at other air pressures (ranging from the atmospheric to 10^4 N/m^2) in the heat and pressure chamber of the installation, and these thermograms differ from the corresponding thermograms of Fig. 1 only in scale; the shapes of the thermograms and the number of critical points do not change with a change in the pressure and temperature of the air within the indicated limits.

Since the moisture from the disperse bodies, on drying, evaporates in the sequence determined by the intensity with which it is bound to the body, for the purposes of this study we need know not only the maximum quantities of moisture in various forms and kinds of bond with the specimens, but also the energy binding the moisture. For all of the investigated specimens with the exception of the quartz sand, we therefore also determined the intrinsic moisture binding energy. The measurements were carried out in the installation [10] according to the method of specific heat of evaporation, with the intrinsic binding energy defined as the difference between the specific heat of moisture evaporation from the body for a given moisture content and the heat of evaporation for the free water. For clarity, the results that we obtained are shown in Fig. 2 together with the corresponding thermograms. To retain the shapes of the thermograms, time has been plotted in Fig. 2 along the axis of abscissae in accordance with the test in which the thermograms were recorded. In this connection, the moisture-content scale for those bodies proved to be nonuniform along the axis of abscissae.

An examination of Figs. 1 and 2 reveals the following: the initial horizontal segments of the thermograms (curves a-e in Fig. 1 and curves a_1-d_1 in Fig. 2) correspond to the evaporation, at the beginning of the experiment, of the excess free water above each of the specimens. Then, as the evaporation of moisture in a given form of bond proceeds from these specimens, the temperature differences – reflected by the thermograms – between the specimens and the air diminsh. The limits of moisture evaporation for various states within the pores of the body and for various binding forms can be found on the thermograms in the form of critical points where the shapes of the curves exhibit change (for example, at the point where a convex curve changes into a straight line) [1]. Particularly characteristic in this regard is the thermogram for the MSM silica gel which is a typical capillary-porous body containing moisture in various bond forms (curve a in Fig. 1 and curve a_1 in Fig. 2). In this thermogram we find five critical points corresponding to the evaporation limits for moisture in various forms and kinds of bond. The energogram (curve a_2 in Fig. 2) shows that certain changes in the intrinsic energy with which the moisture is bound to the silica gel [11] correspond to the boundaries for the moisture in various forms of bond.

Unlike the silica gel, quartz sand contains virtually no micropore and adsorbed moisture. Accordingly, the drying thermogram for quartz sand (curve e in Fig. 1) shows only 3 critical points. This thermogram can be presented, as demonstrated in [1], as a special case of the silica-gel thermogram (curve a in Fig. 1), from which the lower segment after critical point 3, corresponding to the evaporation of the moisture in the micropores and of the adsorbed moisture, has dropped away.

TABLE 1. Differential Moisture Adsorbents

Bond form of removed moisture	Maximum quantities of moisture in various bond forms as a % of the dry specimen weight				Thermogram segment between critical points
	MSM silica gel	calcium hydrosulfoaluminate	mixture		
			calculated	thermogram data	
1	2	3	4	5	6
Micropore moisture	14	—	7	8	3—4
Absorbed moisture in many layers	8	—	4	4	4—5
Adsorbed moisture in a single layer	7,5	—	3,7	3	5—6
Moisture in weak chemical bond	—	48	24	22	6 and beyond

Curves b and c in Fig. 1 show the drying thermograms for the calcium hydrosulfoaluminate and the gypseous aluminous cement stone. Unlike the quartz-sand thermograms, these cannot be regarded as special cases of the silica-gel thermogram from which certain segments drop away. An outstanding feature of these thermograms is the presence, at the end, following critical point 6, of an elongated convex segment which is not found on the silica-gel thermogram. On the other hand, the energograms for these specimens (curves b_2 and c_2 in Fig. 2), after evaporation of the free water, i.e., beyond the first critical point of the thermograms, rise upward steeply and then, near the moisture content corresponding to the sixth critical thermogram point, gradually change into horizontal straight lines. Hence it follows that beyond critical point 6 on the thermogram for these specimens we have the evaporation of moisture exhibiting great and virtually constant intrinsic binding energy with respect to the body, a fact which is characteristic for moisture in chemical bond [5]. The stoichiometric calculation on the basis of the above-presented chemical formula for the calcium hydrosulfoaluminate also confirms that the maximum quantity of moisture in chemical bond with the calcium hydrosulfoaluminate corresponds to the moisture content of the latter at the sixth critical point of the thermogram (about 48%).

We see from the above that critical point 6 corresponds to the onset of evaporation for the moisture retained in the body by weak chemical forces, and beyond that critical point the drying thermogram changes from a concave to a convex line.

Of greatest practical interest is the investigation of disperse bodies containing moisture in various forms of bond including chemically bound moisture. As a typical model of a disperse body containing moisture in all forms and kinds of bond, here we have chosen the above-described mixture of MSM silica gel and calcium hydrosulfoaluminate. The differential water-retaining properties of each of the components in this mixture are well known, and this makes it possible to calculate in advance the quantity of water for each form of bond in the mixture. Table 1 shows the results of the calculation (column 4), as well as the original data for each of the components (columns 2 and 3). We see from the table that the selected mixture of the MSM silica gel and the calcium hydrosulfoaluminate contains substantial quantities of both capillary and adsorbed moisture, as well as moisture in weak chemical bond.

The drying thermogram for such a mixture is shown by curve d in Fig. 1. The upper portion of this thermogram completely reproduces the silica-gel thermogram (see curve a, Fig. 1), but at the very end it exhibits an additional convex segment separated by critical point 6. With the aid of the weight curve, recorded simultaneously with the thermogram (not shown in Fig. 1), we determined the moisture contents for each of the critical points of thermogram d and the quantities of moisture removed in each segment of the thermogram. These data are also shown in Table 1 (columns 5 and 6). A comparison of the figures in the table shows that the moisture contents corresponding to individual segments of thermogram d in Fig. 1 are in good agreement with the calculated quantities of moisture for the corresponding forms and kinds of bond in the given model body. Here a slight increase in the quantity of micropore moisture in the specimen relative to the quantity calculated is apparently explained by the existence of additional pores between the crystalline particles of the hydrosulfoaluminate powder, which had not been taken into consideration in the calculations (see column 3 of Table 1).

Thus thermogram d in Fig. 1 essentially shows the sequence of evaporation for moisture in various forms of bond from the mixture of the MSM silica gel and the hydrosulfoaluminate. This evaporation sequence is also confirmed by the energogram of that mixture (curve d_2 in Fig. 2), measured in the same way as for the pure components. On the energogram we can find three virtually horizontal segments. The first of these corresponds to the evaporation of the free water; the second segment corresponds to the microcapillary moisture removed between the third and fourth critical points of the thermogram, and finally, the third segment which, in terms of the magnitude of the binding energy, substantially different from that of the second segment, corresponds to the evaporation of moisture in weak chemical bond. In this case, the binding energy for the capillary and chemically bound moisture removed at the cited segment of thermogram d (Fig. 1) is very close to the values of the binding energy for moisture of the same bond forms in pure components (see curves a_2 and b_2 in Fig. 2). Of particular significance in this case is the fact that the intrinsic binding energy of the moisture held by weak chemical forces in calcium hydrosulfoaluminate (see curve b_2, Fig. 2) is greater than the binding energy for the moisture adsorbed in the silica gel (see curve a_2 in Fig. 2). The evaporation of virtually all of the adsorbed moisture from the mixture therefore occurs earlier (the segment of thermogram d between critical points 4 and 6) than the evaporation of the chemically bound moisture (the segment of that thermogram beyond critical point 6).

It follows from the above that the classification of weakly bound moisture in a disperse body in terms of the forms and kinds of bond, based on the drying thermogram of the MSM silica gel [1], is insufficiently general, since it does not take into consideration the possible existence within the body of moisture in weak chemical bond, this moisture also being evaporated during the drying period. The drying thermogram for the mixture of the MSM silica gel and the calcium hydrosulfoaluminate thermogram (d in Fig. 1) is more general, and here, at the end of the thermogram, we find yet another convex segment beyond critical point 6, corresponding to moisture in weak chemical bond. The more complete classification of weakly bound moisture according to the forms and kinds of bonds with disperse bodies can therefore be based on the curves of drying kinetics (the thermogram and drying curve) of a thin layer of the model body formed by the mixture of the MSM silica gel and calcium hydrosulfoaluminate.

Such a classification is shown in Fig. 3; it differs from that described in [1] in the fact that there is an additional segment g at the end, which corresponds to the evaporation of moisture in chemical bond.

The form of the thermogram in Fig. 3 is typical of disperse bodies containing moisture in each of the above-enumerated forms and kinds of bond. In particular, such a thermogram is characteristic of certain cement stones containing moisture in weak chemical bond [12]. However, for disperse bodies in which a given form of bond is absent, the corresponding segments disappear from the general thermogram of Fig. 3. As an example we can cite any of the thermograms in Fig. 1. In particular, the thermogram for the gypseous aluminous cement stone (c in Fig. 1) is characterized by an extremely small segment between critical points 3 and 6, which testifies to the small quantity of moisture in the microcapillaries and to the small quantity of adsorbed moisture in this specimen.

The joint analysis of the drying thermograms and energograms for thin specimens of various capillary-porous disperse bodies experimentally confirms the realtionship between the successive removal, through drying, of moisture in various forms and kinds of bond and the various binding energies linking the moisture to the body. Thus the drying-thermogram method in conjunction with the more general proposed method of interpreting the thermograms (Fig. 3) makes it possible, from the results of a single experiment, not only to determine the differential water-retaining properties of the disperse bodies with respect to moisture in physicomechanical and physicochemical bond, but also to determine the quantity of moisture retained within the body by weak chemical forces, i.e., the quantity of moisture in chemical bond.

In conclusion, we should point out that the proposed moisture classification based on the drying thermogram and energogram not only does not contradict the moisture classification based on bond form – as proposed by Academician Rebinder [5] – but rather refines it through additional detailing of individual forms of moisture, with consideration given to the differences between the binding energies of that moisture.

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