DESICCATION THERMOGRAMS FOR DISPERSE
MATERIALS MOISTENED WITH VARIOUS LIQUIDS

III. DESICCATION THERMOGRAMS FOR HYDRAULIC CEMENTS

M. F. Kazanskii, V. M. Kazanskii,
and R. V. Lutsyk

It is shown how the fine-porous structure and the sorption characteristics of various grades of hydraulic cement can be analyzed by the method of desiccation thermograms with the use of several different liquids.

It has been shown in [1, 2] that the fine-porous structure and the sorption characteristics of capillary-porous and colloidal capillary-porous masses can be closely analyzed by the method of desiccation thermograms with the use of several different moistening liquids. The objects of this study here are the desiccation thermograms for hydraulic cement of various mineral compositions and moistened with several different liquids.

Hydraulic cement, unlike other disperse materials, can simultaneously retain not only capillary and adsorbed water, which is typical of brittle and elastic gels, but also appreciable amounts of interlayer water held within the crystal lattices as well as of weakly chemically bonded water (crystal hydrating water) [3] which actively participates in heat and mass transfer processes during the cure and the subsequent useful life of concrete.

The authors selected for the study four grades of hydraulic cement with different chemical compositions and different porosity structures. The Portland cement specimens were made of high-grade M 400 alite from the Amvrosiev Works with 3% gypsum added during grinding. The slag cement specimens were prepared from ground converter slag. The slag—Portland cement specimens were prepared from a mix containing 30% Portland cement, 70% converter slag, and 3% gypsum, all ground together. Finally, the expansive gypsum—alumina cement specimens were prepared from a mix containing 70% alumina and 30% gypsum. All the mortar material was ground down to a specific surface of 3200 m^2/kg, then slaked to a water/cement ratio corresponding to a paste of normal density, and was examined throughout an aging period of one-and-a-half years.

For comparison, we also examined two ingredients appearing in the stone structure in various amounts: pure highly-hydrated calcium hydrosulfoaluminate with weakly bonded moisture and tobermoritic calcium hydrosilicate. Specimens of the former were prepared by mixing appropriate amounts of tricalcium aluminate and gypsum with excess water. The exact correspondence of this formulation to ettringite was ascertained by x-ray and thermographic analyses. Tobermorite was produced by treating silica gel with a calcium hydroxide solution for a long period of time [4].

Isotherms of water vapor desorption were plotted for all specimens, except those of calcium hydrosulfoaluminate, as shown in Fig. 1. The measurements were made with an apparatus [5] which did not require preliminary evacuation and desiccation of a specimen for the plotting of isotherms, thus eliminating any error which would result from the removal of some weakly chemically bonded water and from the breakdown of some crystal hydrates in the structure during evacuation. On the basis of these isotherms, we then calculated the integral pore distribution curves (without correction for the thickness of the adsorptive layer) also shown in Fig. 1 and the moisture capacity of the adsorptive monolayer according to the BÉT method [6]. These data adequately described the microporous structure of the given specimens with respect to water.
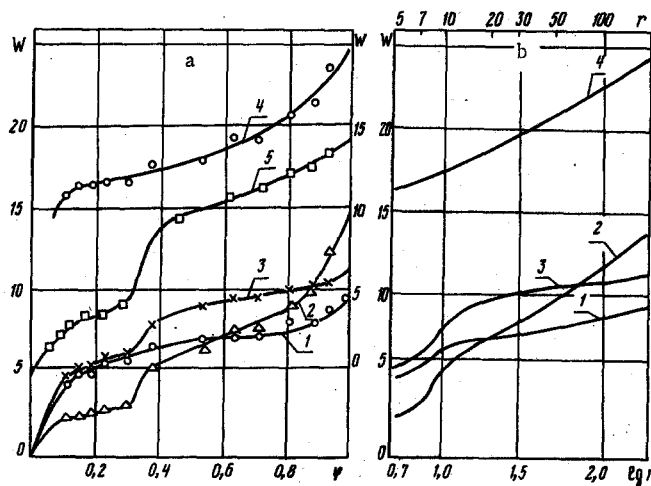
Fig. 1. Water vapor desorption isotherms (a) and integral pore distribution curves (b) for hydraulic cement grades: 1) Portland cement; 2) slag cement; 3) slag −Portland cement; 4) expansive gypsum−alumina cement; 5) tobermoritic cement. Moisture content W (%), relative vapor pressure φ, pore radius r ($\times 10^{-10}$ m).

The thermograms and the kinetics curves were taken with instruments described in [7]. The method of moistening the specimens with various liquids and the test conditions have also been described thoroughly in [1, 2]. It must be emphasized that the desiccation thermograms and the desorption isotherms for the specimens containing water were determined without preliminary desiccation of those specimens, which made it possible to examine the undistorted natural structure of hydraulic cement.

The moisture content was referred to the standard dry weight in each case, the latter determined by predesiccation under atmospheric pressure. The predesiccation temperature here was selected, depending on the air humidity within the 368-388°K range, so that the equilibrium dehydration level should always be the same and equal to the free energy $0.8 \cdot 10^6$ J/kg of a moisture bond [8].

The desiccation thermograms for the hydraulic cement specimens moistened with various liquids are shown in Fig. 2, and the moisture content levels corresponding to the critical points on these thermograms are given in Table 1. As in [1, 2], here the moisture content is given only for the critical points on the lower portion of the thermograms, which correspond to the microporous structure of the test specimens.

It is quite evident here that the shape of a thermogram for the same specimen depends largely on the kind of moistening liquid. This stands to reason, because hydraulic cement is a fine−porous disperse material whose micropores are not always accessible to molecules of the moistening liquid. Furthermore, the shape of a thermogram is also affected by differences in polarity and by other physicochemical properties of the moistening liquid. The curves in Fig. 2 indicate also some differences between thermograms for different cement grades moistened with the same liquid, which must be attributed foremost to the differences in their pore structures.

Portland cement has the smallest pores of all. Relative to water, the volume of its micropores with a radius within the (10-200) $\cdot 10^{-10}$ m range amounts to 2.5% (Fig. 1). Accordingly, only water thermograms (Fig. 2a) exhibit here a short segment between critical points 3 and 4 corresponding to capillary condensation in micropores [1]. For Portland cement moistened with any other liquid, the critical points 3 and 4 on its thermograms merge. This indicates that the fine pores in Portland cement, when the latter is moistened with liquids whose molecules are larger than those of water, become completely filled during adsorption and no capillary condensation occurs in them. The volume fraction, relative to water, of micropores with a radius larger than $20 \cdot 10^{-10}$ m, is largest in slag cement (Fig. 1). Accordingly, on the water thermogram for this specimen there appears a distinctly curved segment 3-4 (Fig. 2b). This segment becomes much shorter for slag cement moistened with methanol and vanishes entirely when slag cement is moistened with other liquids (curves 3b-6b) whose molecules have large effective diameters.
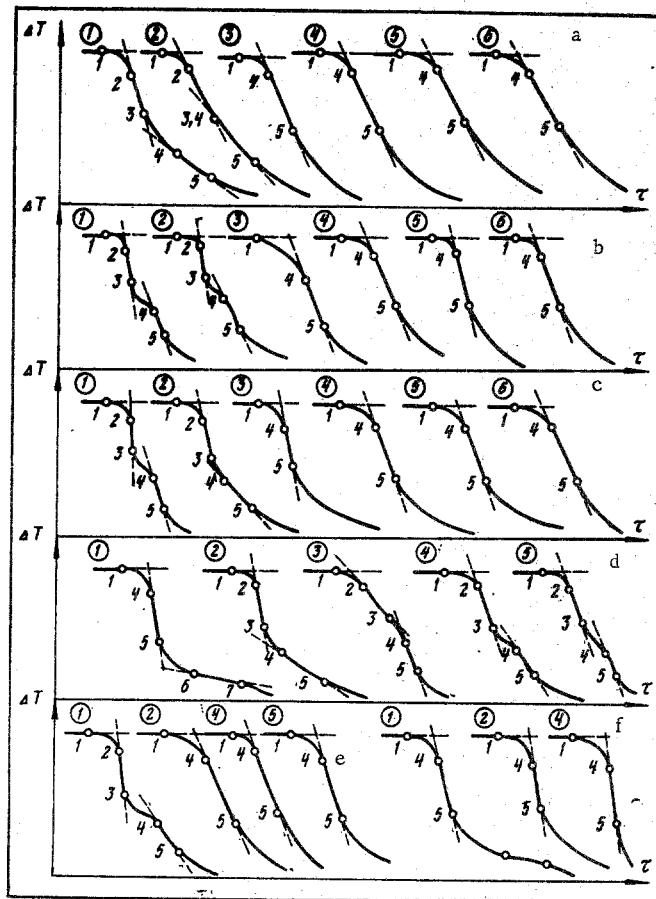
Fig. 2. Typical desiccation thermograms: a) Portland cement; b) slag cement; c) slag–Portland cement; d) gypsum–alumina cement; e) tobermoritic cement; f) highly-hydrated calcium hydrosulfoaluminate, moistened with water (1), methanol (2), butanol (3), benzene (4), cyclohexane (5), heptane (6); difference between specimen temperature and ambient temperature ΔT; testing time τ.

A similar trend is seen in the thermograms for slag–Portland cement (Fig. 2b), which in terms of porosity ranks intermediate between the Portland and the slag grade. Moreover, the volume fraction of pores with a radius larger than $10 \cdot 10^{-10}$ m is smaller in slag–Portland cement than in slag cement and is approximately the same as in the least porous Portland cement.

Thus, a comparison between the shapes of the respective thermograms for Portland cement and slag cement indicates clearly the effect of molecule size in the moistening liquid on the bond mechanism (capillary or adsorption). Slag cement and slag–Portland cement yields thermograms of almost the same shape, on the other hand, despite the much higher porosity of slag cement within the $(30-200) \cdot 10^{-10}$ m range, where capillary condensation not only of water vapor but also of other vapors whose liquid molecules are much larger (cyclohexane with a diameter $6.3 \cdot 10^{-10}$ m and n-heptane with a diameter $6.8 \cdot 10^{-10}$ m) is possible. The difference between the thermograms for slag–Portland cement and slag cement is that in the latter (when moistened with water) the 3-4 segment becomes somewhat longer. This difference may, perhaps, be due to the higher tobermorite content in slag cement, the water absorption characteristics here being related to the crystal structure.

Tobermorite crystals are lamellar. For this reason, water molecules can penetrate between tobermorite stacks and cause the corresponding lattice parameter to increase by $9.4 \cdot 10^{-10}$ m [7]. The absorption of such a water interlayer is reflected on the water adsorption isotherm for tobermorite by a characteristic vertical segment at $\varphi = 0.35$, which corresponds to an effective pore radius also of about $10 \cdot 10^{-10}$ m [4]. Although nuclear-magnetic-resonance measurements have shown that the mobility of absorbed water

TABLE 1. Moisture Content Levels Corresponding to Critical Points on the Desiccation Thermograms, and Adsorption Characteristics of Specimens

Specimen	Moistener	Moisture content level at critical points on thermograms, %			Specific surface, m²/kg			Moisture capacity of monlayer, based on adsorption therms, %	
		W_3	W_4	W_5	S_s	S_1	S_2	a_1	a_2
Portland cement	Water	7,7	7,0	6,6	231	143	143	4,2	4,2
	Methanol	4,3	4,3	3,6	123	—	—	—	—
	Butanol	—	2,7	2,4	57	—	—	—	—
	Benzene	—	3,5	2,2	52	—	—	—	—
	Cyclohexane	—	1,8	0,8	21	—	—	—	—
	Heptane	—	1,1	0,8	27	—	—	—	—
Slag cement	Water	7,5	3,7	2,6	91	77	81	2,2	2,3
	Methanol	4,6	2,4	1,6	56	—	—	—	—
	Butanol	—	2,2	1,1	26	—	—	—	—
	Benzene	—	2,5	1,2	28	—	—	—	—
	Cyclohexane	—	2,2	1,1	28	—	—	—	—
	Heptane	—	1,5	0,9	41	—	—	—	—
Slag–Portland cement	Water	10,4	8,1	6,2	217	168	157	4,8	4,5
	Methanol	3,5	2,9	2,4	82	—	—	—	—
	Butanol	—	1,7	1,5	36	—	—	—	—
	Benzene	—	1,9	1,2	28	—	—	—	—
	Cyclohexane	—	1,8	0,8	21	—	—	—	—
	Heptane	—	1,9	1,1	34	—	—	—	—
Gypsum –alumina cement	Water	—	20,0	19,0	665	560	300	16,0	8,5
	Methanol	4,4	4,4	3,1	106	—	—	—	—
	Butanol	3,0	2,1	1,9	45	—	—	—	—
	Benzene	6,7	4,3	2,5	59	—	—	—	—
	Cyclohexane	7,0	1,6	0,8	21	—	—	—	—
Calcium hydrosulfoaluminate	Water	—	—	49,0	1730	—	—	—	—
	Methanol	—	13,2	4,2	143	—	—	—	—
	Butanol	—	9,3	1,5	35	—	—	—	—
Tobermorite	Water	9,5	4,8	2,7	95	—	—	—	—
	Methanol	—	5,4	3,2	109	—	—	—	—
	Benzene	2,9	2,2	0,9	21	—	—	—	—
	Cyclohexane	—	2,5	1,2	31	—	—	—	—

is closer to that of adsorbed water than to that of capillary water [9], all the thermodynamic properties of that adsorbed correspond nevertheless to the capillary bond mechanism [10]. Inasmuch as interlayer water evaporates at a constant bond energy, this evaporation is reflected on the desiccation thermogram by a characteristically even more convex 3-4 segment [11] (curve 1e in Fig. 2) than in the case of slag cement or slag–Portland cement. Molecules of other liquids do not penetrate at all into the interlayer structure of tobermorite and, therefore, no 3-4 segment appears on the curves 2e and 4e in Fig. 2.

A steep segment on the adsorption isotherm at $\varphi = 0.35$, which is characteristic of tobermorite, appears also on the isotherms for slag cement and slag–Portland cement (Fig. 1), but it reflects only a part of the total micropore volume in these specimens. For this reason, the thermograms for these specimens change when water is replaced by methanol but not as much as in the case of pure tobermorite.

Another trend is noted on the desiccation thermograms for pure calcium hydrosulfoaluminate and for expansive gypsum–alumina cement, the latter material containing approximately 40% of the former. Calcium hydrosulfoaluminate crystals retain water by rather weak chemical forces, and during desiccation down to the free bond energy level of $0.8 \cdot 10^6$ J/kg are broken up while approximately 23 water molecules are released [12] with a corresponding volume reduction. Molecules of the liquids other than water cannot, of course, enter the crystal lattice of calcium hydrosulfoaluminate. For this reason, on thermograms 1d and 1f in Fig. 2 taken for gypsum–alumina cement and for calcium hydrosulfoaluminate, respectively, there appear no 3-4 segments at all which correspond to water evaporation from micropores, but there appear long 6-7 segments which correspond to evaporation of weakly chemically bonded water from crystal hydrates. For gypsum–alumina cement moistened with any of the other liquids, the 3-4 segments appear on the thermogram but not the straight 6-7 segments at the end of the curve. The appearance of micropores in gypsum–alumina cement is in this case related to the drying it must undergo prior to its subsequent moistening with another liquid. Part of the calcium hydrosulfoaluminate crystal hydrates then break up and, as a result, the volume of calcium hydrosulfoaluminate in the cement decreases, while micropores appear which become filled with a given liquid other than water by capillary condensation and the 3-4 segments on the desiccation thermograms d in Fig. 2 correspond to these micropores.

It clearly follows from this discussion that, although the macrostructure of hydraulic cement is rather rigid, the microporous structure may change much during interaction with water. (Analogous concepts have been developed in [14] for the analysis of concrete setting.) It is very important here that the desiccation thermograms taken with various liquids reflect these changes accurately.

The method of desiccation thermograms is very sensitive to the sorption characteristics of hydraulic cement with respect to various liquids. This is most clearly seen upon an analysis of the moisture content levels at critical points 4 and 5 on any desiccation thermogram, which corresponds to the evaporation limits for the adsorbed liquid in monolayers and polylayers of brittle gels [1]. These data are given in Table 1. Table 1 also lists the moisture content levels a_1 determined from desorption isotherms at a relative vapor pressure $\varphi = 0.1$, usually considered the boundary level for an adsorptive monolayer [15], and also the moisture capacities of an adsorptive monolayer a_2 determined according to the BÉT method. For all moisture parameters (a_1, a_2, and W_5) we also calculated the respective specific surface of the solid phase S_1, S_2, and S_5 [6]. The area occupied by one molecule of another liquid was determined here according to the formulas in [6].

An examination of these tabulated data reveals, first of all, a regular decrease in the specific surface S_5 of all specimens as the liquid molecules become larger. This is particularly pronounced in the case of fine-porous Portland cement and to a lesser extent but still appreciably in the case of coarse-porous slag cement.

Our value for the specific surface S_5 with respect to benzene agrees closely with most published data on the specific surface of cement according to low-temperature nitrogen adsorption [16, 17] for Portland cement and for slag—Portland cement, but is approximately 4-5 times lower with respect to water.

The very large specific surface of Portland cement and slag—Portland cement according to desiccation thermograms and adsorption isotherms for specimens moistened with water cannot be explained by the small size of water molecules alone (as was attempted in [18, 19], for instance) or by the effect of chemosorption alone (as was attempted in [20]). Physical adsorption is quite probably aided here by various bond mechanisms, among which a water bond is easily broken up by crystal hydrates (weakly chemically bonded water [13]) and plays an important role. Examples are gypsum—alumina and pure calcium hydrosulfoaluminate, which yield very large specific surfaces S_5 with respect to water while containing almost no micropores. At the same time, slag cement containing no gypsum and thus no calcium hydrosulfoaluminate yields a much smaller specific surface with respect to water. Large amounts of "unstable" hydrating water, i.e., water which together with adsorbed water participates in mass transfer to the ambient medium, have also been revealed in Portland cement by nuclear-magnetic-resonance measurements [21].

The effect of weakly chemically bonded water (in crystal hydrates) can also be the reason why the moisture capacity of an adsorptive monolayer a_1 according to the BÉT method for Portland cement, slag —Portland cement, and especially for gypsum—alumina cement does not match with the moisture content level W_5 corresponding to critical point 5 on the thermograms, while for slag cement both values come close (see Table 1). The BÉT equation for slag cement and for slag—Portland cement is satisfied formally only, moreover, inasmuch as the values of parameter C become anomalously high (above 400) and indicate correspondingly high values of bond energy, which are unconfirmed by direct measurements [22, 23]. For gypsum—alumina cement, on the other hand, the test points on isotherms in BÉT coordinates fit on a straight line, but parameter C becomes negative and this is physically absurd altogether.

Thus, water absorption in hydraulic cement differs strongly from the adsorption of other liquids, owing to the small size of water molecules and the related-to-it"molecular sieve" effect, and also owing to the special andpeculiar-to-water-only mechanisms of bonding it to the solid phase (weak chemical bond or interlayer absorption in a crystal lattice, for example). In order to obtain sufficient information about the pore structure and the specific surface of the solid phase in hydraulic cement, therefore, it is necessary to make measurements with water and at least one other liquid. A nonpolar liquid such as benzene, for example, is best used as that second kind of adsorbate.

The results of this study indicate that such measurements with two or more liquids can be made on the same apparatus by the method of desiccation thermograms. In a study of hydraulic cement, this method offers great advantages over equilibrium methods in terms of a shorter testing time and thus the feasibility of examining the material structure during its actual formation [22].

LITERATURE CITED

1. V. M. Kazanskii, R. V. Lutsyk, and A. F. Mel'nikova, Inzh.-Fiz. Zh., 22, No. 2 (1972).
2. M. F. Kazanskii, V. M. Kazanskii, R. V. Lutsyk, and A. F. Mel'nikova, ibid., 23, No. 3 (1972).
3. K. G. Krasil'nikov, Dokl. Akad. Nauk SSSR, 149, No. 4, 891 (1963).
4. K. G. Krasil'nikov, ibid., 143, 911 (1962).
5. A. I. Chuprina and G. K. Filonenko, Certificate 185481, Byull. Izobret., No. 17 (1966).
6. S. Grég and K. Sing, Adsorption, Specific Surface, and Porosity [Russian translation], Mir, Moscow (1970).
7. M. F. Kazanskii, R. V. Lutsyk, and V. M. Kazanskii, in: Heat and Mass Transfer in Disperse Systems [in Russian], Nauka i Tekhnika, Minsk (1965), p. 136
8. V. M. Kazanskii, Inzh.-Fiz. Zh., 20, No. 5, 787 (1971).
9. G. Englert and F. Wittmann, Zement–Kalk–Gips, 24, No. 7, 312 (1971).
10. V. M. Kazanskii and V. É. Leirikh, Izv. VUZ, Khim. i Khimtekhnol., 13, No. 3, 394 (1970).
11. V. M. Kazanskii, in: Thermal Physics and Heat Technology [in Russian], Vol. 18, Naukova Dumka, Kiev (1970), p. 95.
12. V. M. Kazanskii, Izv. VUZ, Khim. i Khimtekhnol., 14, No. 2, 275 (1971).
13. V. M. Kazanskii, Inzh.-Fiz. Zh., 15, No. 6, 1027 (1968).
14. K. G. Krasil'nikov and N. N. Skoblinskaya, in: Creep and Setting of Concrete [in Russian], NIIZhB Gosstroya SSSR, Moscow (1969).
15. A. V. Lykov, Desiccation Theory [in Russian], Énergiya, Moscow (1968).
16. L. Tomes, C. Hunt, and L. Blaine, J. Res. NBS, 59, 351 (1957).
17. S. Bruwauer, L. Copeland, and R. Bragg, J. Phys. Chem., 60, 112 (1956).
18. H. Rombes, Tonindustr. Zeitung, 95, No. 4, 105 (1971).
19. O. P. Mtshedlov-Petrossian and D. A. Uginchus, Silikattechnik, 20, No. 12, 416 (1969).
20. F. Tamas and G. Sriklai, Epitöanyang, 21, No. 3, 90 (1969).
21. G. Englert, F. Wittmann, and M. Nussbaum, Zement-Kalk-Gips, 60, No. 4, 165 (1971).
22. M. F. Kazanskii and V. M. Kazanskii, in: Problem of Heat and Mass Transfer [in Russian], Énergiya, Moscow (1970), p. 241.
23. V. M. Kazanskii, Inzh.-Fiz. Zh., 6, No. 1, 97 (1963).