ISOTHERMAL VAPOUR ADSORPTION OF PORTLAND CEMENT

by

Z. JUHÁSZ

Department of Building Materials; Technical University, Budapest

(Received February 5, 1973)
Presented by Prof. Dr. J. TALABÉR

If cement, hydrated or not, is kept in humid atmosphere, then it will either bind or bleed water until an equilibrium takes place between the cement and the ambient atmosphere. The equilibrium may be expressed, e.g., as an equality between the tension of the bound water and the partial pressure of the vapour content of the atmosphere, or between the thermodynamical potentials of wet cement and the humid atmosphere. If the partial pressure of the vapour of the atmosphere or temperature of the system changes, also the water content of the cement will change to reach a new equilibrium condition.

In the following, the test results concerning the equilibrium between the non-hydrated or partly hydrated cements and the non-saturated atmosphere at room temperature will be reported. This paper is a preliminary report on the test results obtained by the author and gives no survey on the subject.

1. Test procedure

Products of different cement factories in Hungary and clinker minerals produced by the Department of Silicate Chemistry of the University of Chemical Industry in Veszprém were tested.

3 to 5 g portions of the cement were put in ten graduated jars, and placed for 28 days in desiccator chambers at 23 °C, containing sulphuric acid at different concentrations. On the 28th day they were re-weighed, taking care of the tight sealing of the jars during this operation to protect the specimens against carbon dioxide effect. Equilibrium humidities have been determined from 28-day mass changes ($W\,\% =$ g of water per 100 g of dry specimen). It should be noticed that most cement masses somewhat changed even after 28 days — especially at a higher vapour content — therefore, W was not the actual equilibrium water content, but the "28-day water content" which, however, in the concerned narrow range of humidity, closely approached the state of equilibrium.

Prior to testing, part of the cement samples were hydrated either by steam-curing or by mixing with water, pulverized, and then after 28 days, mass changes over sulphuric acid solutions of different concentrations were weighed. The adsorption of carbon dioxide during pulverization could not be prevented, but this testing error did not interfere with the evaluation.

In the atmosphere of the desiccators, the partial pressure of vapour p may be determined from the concentration of the sulphuric acid solution [1]. The ratio of the partial vapour pressure to the partial pressure p_t of the vapour-saturated atmosphere at the test temperature is the relative humidity $p_r = \frac{p}{p_t}$. Concentrations of the sulphuric acid solutions were checked after every series of densitometry.

For simplifying the evaluation of the test results [2], also derivatograms of some of the specimens were recorded by means of a derivatograph constructed by L. Erdey, F. Paulik and A. Paulik.

2. Processing of test results

Just as the expressions of equilibrium condition referred to introductorily, also equilibria at constant temperature may be represented by the tension curve or the curve of adsorption potential.

1. The *tension curves* represent the correlation between the relative atmospheric humidity p_r and the water content W of the cement (see curve W in Fig. 1), and are, in fact, the isotherms type II of vapour adsorption of the cement, with points of inflexion according to the classification in [3]. To the left of the point of inflexion, in the range of low humidity, the water is purely physically adsorbed on the surface of the particles whilst to the right, water will be bound in the fine pores of the adsorbent by capillary condensation [4].

According to the BET theory [5], the adsorbing layer may also be a polymolecular one, however, the second layer of molecules begins only to develop at a higher gas pressure when the first — monomolecular — layer has already completely developed at the lower pressure. The water content W_m of the monomolecular layer may be obtained from the BET equation:

$$\frac{p}{W(p_t - p)} = \frac{1}{W_m c} + \frac{c-1}{W_m c} \cdot p_r = b + mp_r$$

where c is the adsorption constant: b and m are graphically determined values. From the surface area covered by a single molecule of water (10.8 Å^2), [6] and from W_m the specific area Ω referred to the vapour adsorption may be calculated. Replacing the constants:

$$\Omega = 36.15\ \mathrm{W}_m\ [\mathrm{m}^2/\mathrm{g}]\,.$$

It should be noticed that the hydrated cements give off water in lower humidity ranges (see curve W^1 in Fig. 1), and intersect the W axis at D, a negative value. In this case the curve W^1 has been transformed by superposing D to all its values. Thus, a curve W was obtained, starting at the origin and — to distinguish it from the *adsorption* isotherm representing purely water adsorption — it has been called *desorption* isotherm.

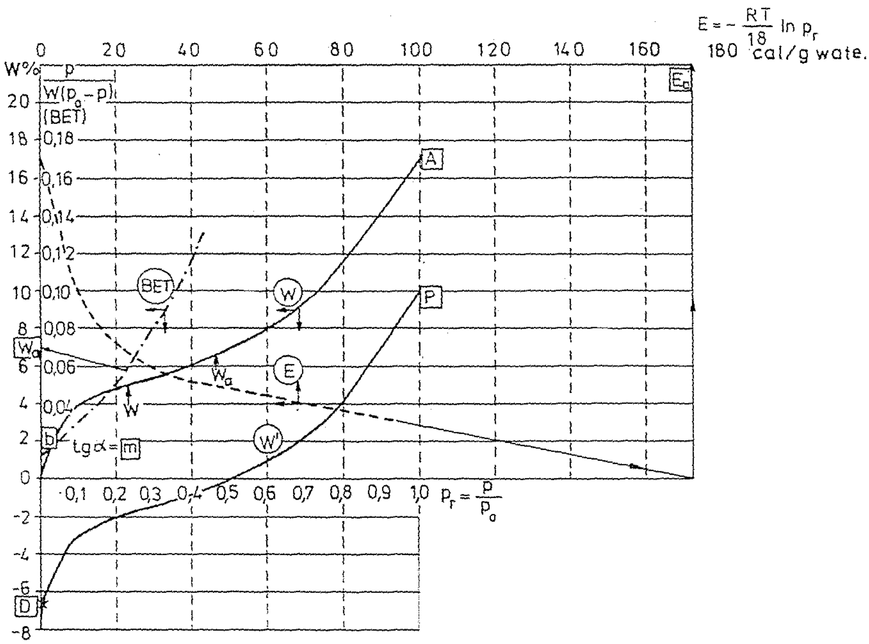

Fig. 1. Tension curves and adsorption potential curves of cement. BET equation applied to the tension curves and graphical evaluation of the potential curves

On the basis of the capillary condensation section, the fine porous structure of the adsorbent might be characterized by the pore-size distribution [4] since at a given humidity, there is only capillary condensation in pores smaller than those described by Kelvin's equation. But, in our case water bond not only by capillary condensation but also by chemical interaction had to be reckoned with (see below). Therefore, no such a "capillary analysis" has been made.

2.2 Another method of representation of the test results is to plot *curves of adsorption potential* (curve E in Fig. 1). According to [7], the adsorption potential is the function of the temperature and the partial vapour pressure:

$$E = -\frac{RT}{18} \ln p_r \quad [\text{cal/g water}]$$

where

R = gas constant; and
T = Kelvin temperature.

Plotting the equilibrium water content W against the actual adsorption potential E, in the region of pure physical adsorption, i.e., at high E values, the points representing the test results were found to lay along a straight line, representing, in fact, equipotential adsorption. Extending the straight line to the W axis, the point of intersection W_a corresponds to the *adsorption capacity*, i.e. to the theoretically maximum of water adsorbed by pure adsorption, independent of the capillary condensation, possibly forming a polymolecular layer. Extrapolating in the opposite sense, *the adsorption potential* E_a, cut down from the curve of potential, yields the potential energy of the perfectly dry surface to bind water, equally a theoretical value (namely if $p_r \rightarrow 0$ then $E \rightarrow \infty$).

2.3 The critical points of the two kinds of curves delivered the *surface potential* referred to the water adsorption, i.e., the energy of the isotherm bond of water on 1 sq. m area of the cement:

$$E_F = \frac{1}{100\,\Omega} \int_0^{W_a} E\,dW = \frac{E_a W_a}{200\,\Omega}\ [\mathrm{cal/m^2}]\,.$$

3. Measurement data

3.1 *Tension curves of clinker minerals*

Tension curves of the clinker minerals are seen in the left-hand side of Figs 2 and 3. Vapour adsorption is represented by adsorption isotherms from O to A while desorption isotherms in the section from D to P are the tension curves of the hydrated clinker minerals. These latter were plotted from equilibrium water contents determined by keeping the clinker mineral pastes in saturated atmosphere for 28 days, then pulverized and weighed after another 28-day storage over sulphuric acid solutions. The desorption isotherms represent the increment related to heated material.

From 5-month paste samples belonging to points D and P also derivatograms have been plotted, DTG curves being seen at the right-hand side of the figures, with numerals indicating the loss in mass in the represented temperature range, in percentages of the heated material.

The values determined by calculation or graphically from the tension curves are tabulated.

Comparing the *adsorption isotherms* with each other leads to the following conclusions:

a) From among the four clinker minerals, tricalcium silicate has the

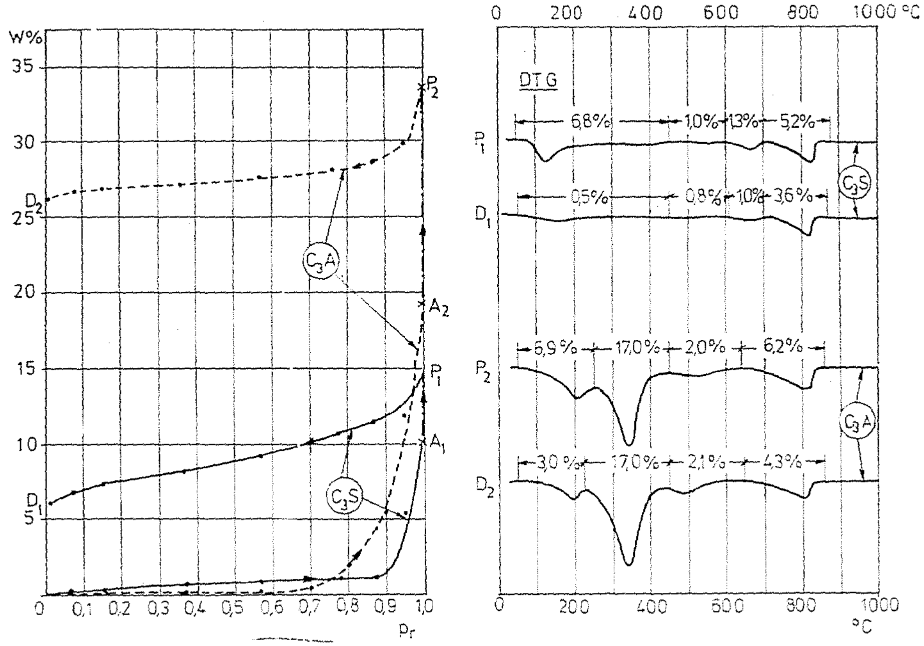

Fig. 2. Tension curves and DTG curves of C_3S and C_3A

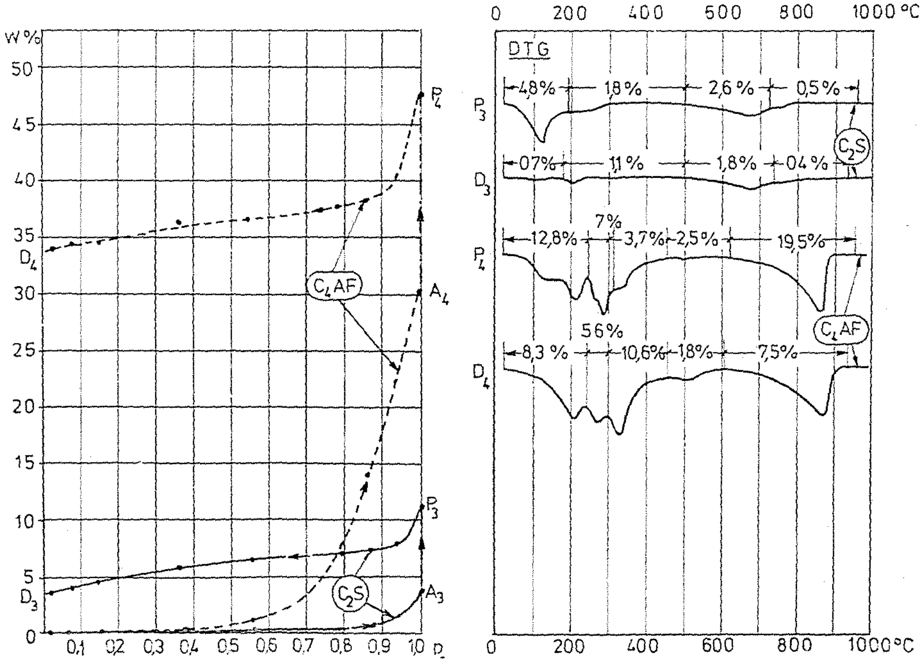

Fig. 3. Tension curves and DTG curves of C_2S and C_4AF

greatest, and dicalcium silicate the smallest *specific surface* also in conformity with the difference between their hydration velocities. On the other hand, from the C_3A and C_4AF, it is the brownmillerite which possesses a very high surface potential. It might be thought that the relatively quick hydration of this latter mineral is associated exactly with its high surface energy.

b) Also the difference between the *capillary condensation* branches of the adsorption isotherms of the four clinker minerals is worth mentioning. On the isotherms of the two calcium silicates, the point of inflexion representing the beginning of the capillary condensation belongs to a very high relative humidity (over 0.85 per cent), and the maximum quantity of water adsorbed by capillary condensation (points A_1 and A_3) is relatively low. Thus, these two minerals contain few submicroscopic pores. On the contrary, the curves of C_3A and C_4AF have their points of inflexion at 0.5 vapour content and both of these materials adsorbed much water from the saturated atmosphere (points A_2 and A_4), attributed to the capillary condensation within the multitude of fine pores and the subsequent quick hydration processes.

Concerning the *desorption isotherms* the following can be stated:

a) The maximum water contents P of clinker mineral pastes at a vapour content $p_r = 1$ always are much higher than the maximum amount of water adsorbed from the vapour of the atmosphere (A values on the adsorption isotherms.) The phenomenon may be explained by the fact that, on the one hand, the water content adsorbed during 28 days is less than that of equilibrium, thus point A is indefinite, and on the other, capillary systems and chemically bound water contents of the clinker minerals previously hydrated at different rates and ways, are significantly different.

b) The desorption isotherms intersect the W axis at the positive point D corresponding to a rather high value. The change in mass D represents theoretically the irreversibly bound water content that cannot be eliminated at normal temperature. Notice, however, that since in the experiments the formation of carbonate could not be avoided during pulverization, therefore the value of D is actually lower by the amount of water released from $Ca(OH)_2$, and higher by the absorbed CO_2 than the theoretical value.

c) The specific surfaces of all clinker minerals multipled upon hydration. It is strongly emphasized that these values are related to the given test conditions, to a period of presumably incomplete hydration.

d) The *surface potential* was observed to increase for clinker minerals C_3S, C_2S and C_3A which justified the above statements, i.e., that these systems did not reach the equilibrium state representing the minimum of the free energy. The surface potential was seen to decrease for the brownmillerite alone.

e) Derivatograms showed the water bound irreversibly to be bound really by a high energy, it released only at a high temperature (the final temperature maximum is already connected to carbonate decomposition). The evaluation of the curves and the explanation of the phenomenon is somewhat uncertain, not only due to the different rates of carbonate development but also to the continued reaction of hydration during recording of the tension curves, and during the several months of subsequent storage in closed vessels, changing the bond energy of water.

3.2 *Tension curves of Portland cements at different degrees of hydration*

Portland cement grade 500, of Beremend, was kept for 28 days over solutions of sulphuric acid whereby the specimens adsorbed different quantities W_0 of water. (The adsorption isotherm was practically the same as that for $W_0 = 0.3$ per cent seen in the left-hand side of Fig. 4.) Again, a cement paste was made at $W/C = 0.293$ and kept for 28 days over water. The pre-treated samples were pulverized, and the tension curves recorded (left-hand side of Fig. 4). Also derivatograms of samples belonging to some points of the adsorption isotherm of the cement were recorded.

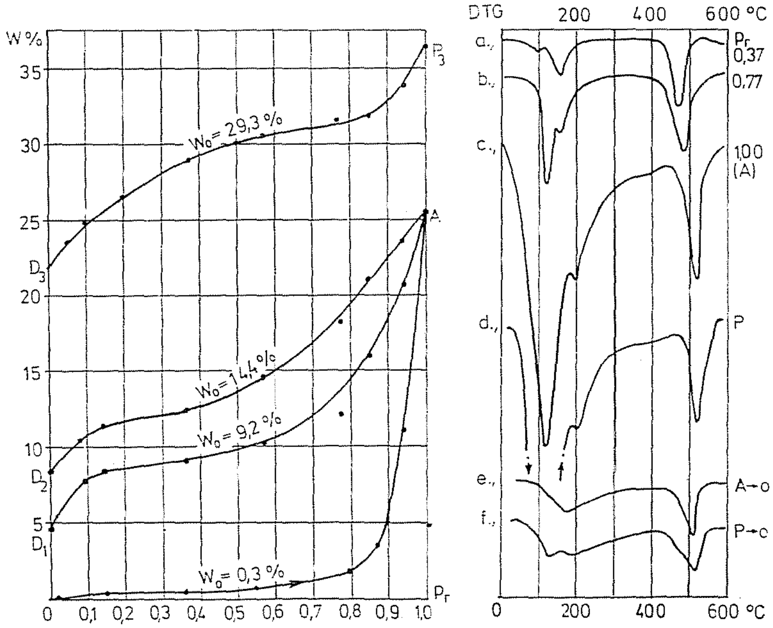

Fig. 4. Tension curves and DTG curves of hydrated cement

The fact that the cement hydration started already during vapour adsorption — in the period of capillary condensation — could be established also from the "coagulation", hardening to a solid skeleton but this process could also be followed on tension curves and derivatograms.

a) Curves *a*, *b* and *c* in the right-hand side of the figure are DTG records of the samples belonging to different points of the adsorption isotherm. Remind that at a low humidity, the bound water is released at a higher temperature, consequently it is bound by a relatively high energy. At a moderate temperature only water bound by less energy, presumably condensed in the capillary pores, will bleed at a higher humidity.

It also is interesting to see that the dissociation temperature of $Ca(OH)_2$ on the curve *a* — thus, at a lower humidity — is lower than that of calcium hydroxide, developed in the presence of much water. This phenomenon can be attributed either to the lower stability of the internal structure or to the higher grade of dispersion of the quoted $Ca(OH)_2$.

The DTG curves denoted by *e* and *f* were recorded by keeping the samples belonging to points *A* and *P*, — i.e. stored and made to paste in a saturated atmosphere — over concentrated sulphuric acid ($p_r = 0$) for 28 days. The cement gave off the major part of its water bound by a smaller energy. The curves of both samples hydrated by two different methods and then dehumidified by desorption are similar, a protracted desorption is likely to bring about identical final states.

b) The *specific surface* of the cement monotonously increased alongside with the amount of water adsorbed during hydration (see Table 1 and Fig. 5), falling short, however, of the specific surface maximum during the tests, in fact, no horizontal section appeared on the specific surface curve.

c) The curve of the *surface potential* has a peak somewhere in the 0.2 to 9.2 per cent range. This means that during adsorption of vapour, the cement gets activated at the critical humidity. This activated state is likely to occur also in the case where excess water is adsorbed, when the hydration processes associated with the reduction of the surface potential are preceded by the intermediate active state expressed by the increase of the surface potential. The activation is connected with capillary condensation, i.e. with the appearance of the water "phase" in the submicroscopic pores with the highest capacity for reaction.

For clarifying the phenomenon further detailed investigations are required.

3.3 *Tension curves of different cements and silicates*

The adsorption and desorption isotherms of some kinds of cements made in Hungary were recorded, tabulating their critical data and calculated values. To help evaluation of specific surfaces related to other minerals, also the adsorption isotherms of a few other silicate minerals were recorded similarly as for cements, and tabulated alike. Concerning the tabulated data, the following should be noticed:

a) The specific surfaces of the cements do not depend on the mineral composition of the clinkers, on the grade of mechanical processing (grinding), crackedness of the particles, etc. alone, but also on the degree of vapour adsorption by the cement prior to the test. With heterogeneous cements — which are not dealt with herein — the specific surface may be affected also by the amount and kind of hydraulic admixture. That is why from the specific surface no unambiguous conclusions can be drawn on the grade of the cement.

Table 1

Data of graphic evaluation and calculation

Test	W_m %	W_a %	E_a cal/g H_2O	Ω m^2g	E_F cal/m^2
Adsorption by C_3S	0.46	0.64	100	16.6	0.0193
Desorption (paste)	2.22	3.00	143	80.3	0.0267
Adsorption by C_2S	0.08	0.12	107	2.9	0.0221
Desorption (paste)	1.16	1.80	114	42.0	0.0244
Adsorption by C_3A	0.12	0.18	100	4.3	0.0210
Desorption (paste)	0.83	1.10	128	30.0	0.0235
Adsorption by C_4AF	0.12	0.24	147	4.3	0.0410
Desorption (paste)	2.12	3.00	162	76.6	0.0317
Portland cement C 500 of Beremend					
Adsorption	0.34	0.56	119	12.3	0.0271
Desorption ($W_0 = 9.2\%$)	4.43	5.30	233	160.1	0.0385
Desorption ($W_0 = 14.4\%$)	4.93	6.40	189	178.0	0.0340
Desorption ($W_0 = 29.3\%$. paste)	6.75	7.60	118	244.0	0.0183
Portland cement C 600 of Tata					
Adsorption	0.39	0.42	112	14.1	0.0167
Desorption ($p_r = 1$)	2.92	4.90	175	106.0	0.0404
Desorption (paste)	4.05	6.15	130	146.5	0.0278
Portland cement C 600 of Vác					
Adsorption sample 1	0.94	1.25	120	33.9	0.0221
Adsorption sample 2	0.64	0.95	106	23.1	0.0231
Portland cement C 500 of Lábatlan					
Adsorption	0.77	0.82	100	27.8	0.0147
Adsorption by high alumina cement	0.39	0.55	124	14.1	0.0242
Desorption ($p_r = 1$)	1.14	1.70	114	41.2	0.0235
Adsorption by ground quarzite	0.15	0.28	143	5.4	0.0370
Adsorption by ground silica gel	14.20	18.90	112	513.0	0.0206
Adsorption by kaolin	1.93	2.4	107	69.7	0.0184
Adsorption by illite	3.09	4.9	99	111.7	0.0217
Adsorption by Ca-bentonite	12.70	21.40	127	459	0.0296
Adsorption by talc	0.05	0.07	55	1.8	0.0011

b) Also in case of the Portland cement grade 600 of Tata, the same difference was observed between surface potentials of steam-cured and of water treated, partly hydrated cements (denoted in the table by "$p_r = 1$", and "paste", respectively).

c) Cement surface potentials are of the order of that for most silicates, their specific surfaces are, in general, less than that of layer lattice silicates, but higher than that of the silicate flour.

Specific surface of hydrated cement is nearly equal to that of illite.

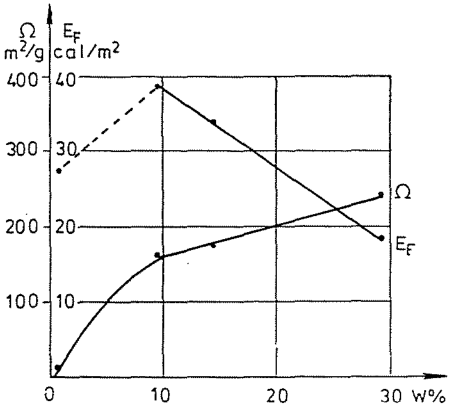

Fig. 5. Specific surface and surface potential vs. water adsorption in hydration

Summary

Vapour adsorption isotherms of clinker minerals and cements lend themselves to calculate the specific surfaces and the surface potentials related to vapour content. Checks were made by means of a derivatograph, and the following conclusions were drawn:

1. The adsorption of vapour is but partly reversible because part of the water is used for the hydration of the cement and is released only at a higher temperature.
2. The specific surface of the cement increases in dependence on the degree of hydration.
3. The specific surface of the cement is greater than that of pure clinker minerals. From among the four kinds of clinker minerals investigated, the tricalcium silicate had the largest, and the dicalcium silicate the smallest specific surface. That of the brownmillerite is small, a high surface potential.
4. During vapour adsorption the surface potential was observed to rise temporarily, considered as an activated state.
5. No unambiguous conclusions can be drawn from the specific surface on the grade (e.g. on the strength) of cement.

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Sen. Ass. Dr. Zoltán Juhász, 1092 Budapest, Kinizsi u. 1—9. Hungary