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ANALYZED

USE OF COMPACTS TO STUDY THE
SORPTION CHARACTERISTICS OF POWDERED PLASTER OF PARIS

BY

R. F. FELDMAN AND P. J. SEREDA

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ANALYZED

USE OF COMPACTS TO STUDY THE SORPTION CHARACTERISTICS OF POWDERED PLASTER OF PARIS

By R. F. FELDMAN and P. J. SEREDA

Compacts made from powdered material are used in an effort to explain anomalous results obtained from the isothermal uptake of water vapour by various types of dehydrated gypsum. In the sorption isotherms, a sharp discontinuity occurred at R.H. between 0.25 and 0.40 and a secondary hysteresis was observed. Sorption of methanol on these materials was also measured, and results were compared with those obtained with water.

The determination of the expansion isotherm enabled an application of the Gibbs adsorption equation to be made, which led to a method by which it was possible to differentiate between hemihydrate and adsorbed water and thus allow a calculation of a B.E.T. surface area from the water isotherm for the material.

From this calculation and others obtained by use of a modified Kelvin equation, it was concluded that the anomalies noted above were due to sites on the surface of the plaster that required an activation energy for 'sorption' to occur. The generation of these sites was considered dependent on the method of preparation of the anhydrous calcium sulphate. The water attached to these sites would thus be termed 'chemisorbed' water.

Introduction

The uptake of water by dehydrated gypsum has already been investigated, but inconsistencies in the results and in the derived hypotheses remain unexplained.¹⁻³

A previous paper⁴ describes the preparation of rigid porous bodies, 'compacts', from powders. The present work describes the use of several types of dehydrated gypsum in the observation of the dimensional changes associated with sorption of water vapour. This has made possible the study of the effect of the decrease of surface free energy and the development of spreading pressure as the adsorbate associates itself with the surface.

Experimental

The apparatus used for this work was designed to expose 12 samples simultaneously to the same vapour pressure conditions. Six were mounted in individual tubes on quartz spirals of the McBain-Bakr type, giving the results of the weight changes to a sensitivity of 2.5×10^{-5} g. for sorption isotherms. The remaining six samples were mounted on modified Tuckerman optical extensometers (see ⁴) and placed in individual cells equipped with optical windows. This procedure yielded dimensional changes to a sensitivity of 2×10^{-6} in./in. with changes in vapour pressure.

A three-stage oil diffusion pump backed by a rotary vacuum pump was employed to reduce the pressure of the system to 10^{-6} mm. Hg or less before adsorbate was introduced from a bulb immersed in a bath that could be controlled at temperatures between 0° and 70°F, within 0.1°F. The samples were maintained at 70°F by immersing the lower ends of the tubes and cells containing them to a depth of 12 in. in a controlled temperature bath. Room temperature was controlled at $73 \pm 1^\circ\text{F}$.

Water-free methanol was introduced into the apparatus, when required, by placing high-purity methanol over calcium oxide in a vacuum-tight vessel which could be attached to the apparatus. The air was then evacuated from the apparatus and the methanol was allowed to remain in contact with the calcium oxide for 48 h. Occasional agitation ensured intimate contact. The methanol was then slowly distilled over into the cold bulb, and kept there as a source of this adsorbate.

Four different types of dehydrated gypsum were studied:

- (i) Pottery plaster—produced by the 'aridised process' consisting of heating gypsum with traces of calcium chloride.
- (ii) Reagent grade precipitated gypsum (Fisher Scientific Co.)
- (iii) 'B-Base' hydrocal—pure gypsum rock dehydrated in the presence of steam (U.S. Gypsum Co.)
- (iv) 'Alba-Floc' dihydrate (U.S. Gypsum Co.), prepared by a precipitation technique.

The samples were made into compacts compressed at 46,400 p.s.i. following the technique outlined by Sereda & Feldman.⁴ Dehydration was achieved by heating the samples at 150°C or 200°C under vacuum of $<10^{-6}$ mm. Hg for 4 h.

For equilibrium to be attained at any one condition along the isotherm, a period of 1–2 days was generally allowed; a 15 h. period of negligible weight change was always allowed to elapse before the system was considered to be in equilibrium.

Results and discussion

Water sorption on calcium sulphate (anhydrous)

(1) *The sorption isotherms*

The sorption isotherms for the four types of calcium sulphate materials were plotted as shown in Figs. 1–6(a). All samples were dehydrated at 150 or 200°C before exposure to the water vapour. In general, the isotherm may be divided into four regions:

(i) That represented by OA shows a large increase in weight at a low relative humidity, mainly due to the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ and the presence of some 'sorbed' water. It may be observed that this point exceeds the theoretical amount of water ($\approx 6.6\%$) required for hemihydrate formation for samples dehydrated at 150°, except that of the 'B-Base', but for samples dehydrated at 200° this point is below the theoretical.

(ii) The region of the isotherms designated AB represents a small amount of water compared with that initially taken up; it is relatively independent of the temperature of dehydration. The amount of water sorbed in this region increases consecutively through 'B-Base', pottery plaster, 'Alba-Floc' and 'precipitated gypsum'.

(iii) At point B a discontinuity in the slope of the isotherm occurs in most cases, followed by a steady rise in the curve from points B to C. This discontinuity occurs for the different samples between p/p_0 values of 0.25 and 0.40, while with the 'B-Base' sample, there are two discontinuities. The effect of the temperature of dehydration on the occurrence of these discontinuities appears to be only a modifying one. In pottery plaster samples the higher temperature of dehydration causes two discontinuities to occur, as compared with one for the lower temperature of dehydration (Figs. 3a and 4a). For precipitated gypsum there appears to be little discontinuity.

(iv) On desorption a hysteresis loop occurs and extends for the whole range of pressures

Fig. 1. Results from compact of 'B-Base' hemihydrate dehydrated at 150°
 (a) sorption isotherms (b) expansion isotherms (c) dimensional change as related to water sorbed
 ○ adsorption □ desorption

Fig. 2. Sorption isotherms for water on compact of 'B-Base' hemihydrate dehydrated at different temperatures
 (a) dehydrated at 200° (b) dehydrated at > 150 < 200°
 ○ adsorption □ desorption

without rejoining the adsorption cycle. Although it never meets the adsorption part of the loop, it levels off and continues almost parallel to the adsorption part of the cycle AB. The extent of the separation between the desorption and sorption curves in the region AB is termed secondary hysteresis and is present to a larger degree in the 'B-Base' and pottery plaster samples than in the other two. This was also observed for the extent of the discontinuities.

(2) *Dimensional changes resulting from water sorption on plaster (expansion isotherms)*

Expansion isotherms for plaster materials can be divided into regions corresponding to those used above for describing the sorption isotherms (Figs. 1, 3—5 and 6b) and have similar characteristics involving the discontinuity and double hysteresis. To represent more clearly the expansion produced by water sorbed at any particular pressure, a plot of sorbed water $\Delta W\%$ vs expansion $\Delta l/l\%$, is shown on Figs. 1, 3—5 and 6(c). O, A, B, C represent the same points as in the previous plots.

Fig. 3. Results from sorption on compact of pottery plaster dehydrated at 150°

(a) sorption isotherms (b) expansion isotherms
 (c) dimensional changes as related to water sorbed
 ○ adsorption □ desorption

Fig. 4. Results from compact of pottery plaster dehydrated at 200°

(a) sorption isotherms (b) expansion isotherms
 (c) dimensional changes as related to water sorbed
 ○ adsorption □ desorption

Four regions are again apparent:

- (i) OA, where hemihydrate formation occurs and where the average slope of the curve of $\Delta l/l$ vs ΔW is the lowest for the whole plot.
- (ii) AB, where a linear plot may be observed and where the slope is at its greatest value.
- (iii) BC, where the slope decreases gradually from B to C in Figs. 3, 4, 6(c), and in Figs. 1 and 5(c) where the slope actually increases over a portion of this region. Nevertheless a transition from AB to BC can always be observed.

Fig. 5. Results from compact of 'Alba-Floc' dihydrate dehydrated at 150°
 (a) sorption isotherms (b) expansion isotherms (c) dimensional changes as related to water sorbed
 ○ adsorption □ desorption

Fig. 6. Results from compact of precipitated gypsum dehydrated at 200°
 (a) sorption isotherms (b) expansion isotherm (c) dimensional changes as related to water sorbed
 ○ adsorption □ desorption

(iv) The desorption loop (in the region BC) for Fig. 6(c) falls below the adsorption loop but rejoins the linear portion AB. Sorption is carried up to a p/p_0 value of 0.83. In Fig. 5(c) the desorption curve does not drop below the adsorption curve, but sorption is continued only to a p/p_0 value of 0.70.

Sorption of methanol on anhydrous calcium sulphate

Having observed unusual characteristics of the isotherm for water it was of interest to learn whether this was specific for water, and an isotherm for methanol on plaster was therefore determined.

A smooth type II isotherm^{4a} was obtained with carefully dried methanol as adsorbate and anhydrous calcium sulphate as adsorbent (Fig. 7b). After early sorption any increase with relative

vapour pressure was very low and a significant increase was observed only at a relative pressure of 0.75 for the sample obtained from dehydrated pottery plaster. For that obtained from dehydrated precipitated gypsum the sorption curve was similar, although greater sorption occurred (Fig. 7a). On the desorption curve, secondary hysteresis was present for both samples, but to a larger extent for the dehydrated precipitated gypsum. It may be seen that very little desorption occurred after a relative pressure of 0.85 for this latter sample, although there was a pronounced hysteresis loop at a relative pressure of 0.56 for the other sample.

The discontinuity observed with water sorption is not present with methanol sorption, although secondary hysteresis is present, to a larger extent for dehydrated precipitated gypsum. Assuming that the methanol molecule occupies an area of $15.2\text{\AA}^2$, an area of $11.4\text{ m}^2/\text{g.}$ was obtained by the B.E.T. method of calculation for the dehydrated pottery plaster sample, and one of $16.7\text{ m}^2/\text{g.}$ for the dehydrated precipitated gypsum. It must be stressed, however, that the methanol isotherms were determined in both cases on the anhydrous calcium sulphate.

Analysis of results

It has been observed for a long time that the water content of plaster of Paris varies and even exceeds the theoretical. Dunn⁵ suggested a series of subhydrates ranging from 0 to $2/3\text{ H}_2\text{O}$, as did Bunn.⁶ Another area of disagreement is provided by the question of whether $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ is a hydrate or a zeolite. Jury & Light³ observed a discontinuity in the isotherm, but this has not received much further attention. The explanation was that further hydration had taken place, and that $12\text{CaSO}_4 \cdot 8\text{H}_2\text{O}$ had been formed from $12\text{CaSO}_4 \cdot 6\text{H}_2\text{O}$. The two extra water molecules were attached to two 'forbidden sites' that required a further activation energy for their hydration.⁶

This explanation has been discounted here. The $\Delta l/l$ vs $W\Delta$ plots (Figs. 1, 3—5 and 6(c)) show three distinct regions, the slope being very low for the region where hemihydrate is formed, and large for the region where the discontinuity is observed. As the two forbidden sites are part of the same structural cell as the others in the $12\text{CaSO}_4 \cdot 8\text{H}_2\text{O}$ unit, a similar expansion for unit weight gain might be expected. This is not the case, however, and it may be concluded that the discontinuity is not due to the formation of a further hydrate.

Fig. 7. Sorption isotherms for methanol on anhydrous calcium sulphate

(a) from precipitated gypsum (b) from pottery plaster
○ adsorption □ desorption

It is possible that this discontinuity is due to multimolecular adsorption and subsequent capillary condensation in small pores, although on this basis a sharp rise at a somewhat similar R.H. should have been observed with methanol as adsorbate. Based on the assumption of capillary condensation, however, the pore size distribution was calculated from the desorption curve for pottery plaster (Fig. 3b) down to the point where it flattened out at a R.H. of 32%. This calculation was made by the use of a modified form of the Kelvin equation,

$$R_i = \frac{2\sigma M}{RT \ln p_0/p} + t \dots\dots\dots (1)$$

where it is assumed that the adsorbate completely wets the solid, and that at any point on the desorption isotherm all pores have an adsorbed film of thickness t , which may vary with pressure of adsorbate p . All pores smaller than radius R_i are completely filled by adsorbed water, and for a filled pore having a radius of R_i the meniscus is assumed to have a radius of $(R_i - t)$. The value of the thickness of the adsorbed layer t as a function of pressure was taken from an estimate by Powers⁷ for cement gel in which it was assumed that the thickness of the strongly adsorbed layer does not exceed two molecular diameters.

The surface area of the adsorbent may be calculated from the pore size distribution by a numerical integration of the area of all the pores. Assuming cylindrical pores,

$$\Delta A_i = 2 \Delta V_i / R_i \dots \dots \dots (2)$$

where ΔA_i and ΔV_i are the area and volume per g. of sample for each group of capillaries taken to have R_i as its corrected mean pore radius. Pierce's method⁸ was used in this calculation; a correction is made for desorption that occurs from the film of larger pores that have already lost their menisci, as well as for the fact that the area obtained is that of the film and not the pore walls.

The cumulative area calculated from the pore size distribution was 34.6 m.²/g. This calculation was made on the sample of pottery plaster, and, since the desorption loop of the dehydrated precipitated gypsum was not very different from that of the pottery plaster, the calculation was not repeated for the other samples, although it was assumed that the result would be similar.

When this result is compared with those obtained from the methanol isotherms by the B.E.T. area calculation, it is found that there is a three-fold difference for pottery plaster and a two-fold difference for dehydrated precipitated gypsum. For a true comparison to be made, however, the area should be calculated from the water isotherm by the B.E.T. procedure. As can be seen from the first point obtained on the water isotherms of Figs. 1—6(a), the weight gained varied from 7.0% for the 150°-dehydrated sample of 'Alba-Floc' dihydrate to 4.20% for the 200°-dehydrated sample of B-Base hemihydrate. This makes it impossible to calculate the surface area of the samples by the B.E.T. method from the water-vapour isotherms; clearly, one cannot determine what portion of the water first taken up is used for the formation of the hemihydrate and what portion is physically adsorbed.

A method based on the Gibbs adsorption equation has been worked out here to estimate the quantity of the sorbed water and thus allow a calculation of the area by the B.E.T. method. This equation relates the lowering of the surface free energy, ΔF , as sorption occurs on a surface, as follows

$$\Delta F = RT \int_0^p s/p \cdot dp \dots \dots \dots (3)$$

where p is the pressure of the adsorbate in dynes/cm.², and s is the surface concentration of adsorbate on adsorbent in g. mols./cm.². When ΔF is calculated by graphical integration, a plot of $\Delta l/l$ vs ΔF should, according to the Bangham relation,⁹

$$\Delta l/l = \lambda \Delta F \dots \dots \dots (4)$$

yield a straight line through the origin. $\Delta l/l$ is the expansion due to sorption and λ is a constant related to the elastic coefficient of the material. All the values required for these plots are known except the absolute values for the weight gain and dimensional change due to sorption, and the B.E.T. surface area calculated from the water sorption isotherm.

The samples at approximately 10% humidity may be considered as CaSO₄·0.5H₂O as adsorbent with some water present as adsorbate. If it were possible to remove this adsorbed water without decomposition of the hemihydrate, the dimensional change $\Delta l/l(A)$ resulting from the adsorption of water $\Delta W(A)$ and the dimensional change $\Delta l/l(H)$ from hemihydrate formation $\Delta W(H)$ would be known. Considering these expansions and weight gains as independent of one another we have the equations

$$\Delta l/l(H) + \Delta l/l(A) = \Delta l/l(T)$$

$$\Delta W(H) + \Delta W(A) = \Delta W(T)$$

where $\Delta l/l(T)$ and $\Delta W(T)$ are the actual weight gain and dimensional change observed.

Since no further hemihydrate formation will take place beyond approximately 10% humidity, line AB on the $\Delta l/l$ vs ΔW plot (Figs. 1, 3, 4, 5, 6c), which is approximately linear,

is a relation between $\Delta l/l(A)$ and $\Delta W(A)$. This same plot for other adsorbents, e.g. Vycor glass¹⁰, calcium carbonate and Cab-O-Sil silica⁴ for low coverages from no adsorbed water to one or two molecular layers, shows a linear portion through the origin.

It may thus be concluded that if the linear portion AB were extrapolated back, this line would pass through the point where both $\Delta W(A)$ and $\Delta l/l(A)$ are zero. The residual $\Delta W(T)$ and $\Delta l/l(T)$ would be equal to $\Delta W(H)$ and $\Delta l/l(H)$ as seen from the above equations. A trial and error procedure is used by taking any point on this extrapolated line as the zero for $\Delta W(A)$ and $\Delta l/l(A)$, calculating the B.E.T. area and determining ΔF from the Gibbs equation for several p/p_0 values; a plot of $\Delta l/l$ vs ΔF did yield a straight line; this procedure was repeated until a straight line through the origin was obtained (Fig. 8). The values obtained from this are shown in Table I.

A value for Young's modulus for the plaster may be calculated from another relation from Bangham & Maggs,⁹

$$E = \rho A / \lambda \dots \dots \dots (5)$$

where ρ is the density (g./c.c.), A is the internal surface area (cm.²/g.) and λ is the constant as in equation (4).

Fig. 8. Expansion of compacts of plaster as a function of the calculated spreading force

□ dehydrated precipitated gypsum ▲ pottery plaster dehydrated at 150°
○ pottery plaster dehydrated at 200° ● dehydrated 'Alba-Floc' dihydrate
△ dehydrated 'B-Base' hemihydrate (numerals on curves are p/p_0 values)

Table I

	Dehydration temperature, °C	Expansion due to hemihydrate formation, %	Weight gain due to hemihydrate formation, %	E , dynes/cm. ²	B.E.T. area from methanol isotherm, m. ² /g.	Kelvin equation area, m. ² /g.	B.E.T. area from water isotherm, m. ² /g.
Pottery plaster A	150	0.060	6.60	1.06×10^{10}	11.4	34.6	12.3 (W_m^* at p/p_0 of 0.22)
Pottery plaster B	200	0.062	5.62	1.31×10^{10}	—	34.6	11.1 (W_m^* at p/p_0 of 0.22)
Dehydrated precipitated gypsum	200	0.10	5.68	2.15×10^{10}	16.7	34.6	34.1 (W_m^* at p/p_0 of 0.31)
'B-Base' hemihydrate	150	0.090	5.53	1.34×10^{10}	—	—	5.0 (W_m^* at p/p_0 of 0.21)
'Alba-Floc' dihydrate	150	0.16	6.62	5.87×10^{10}	—	—	25.10 (W_m^* at p/p_0 of 0.25)

*Weight of water required for one complete monolayer on the surface of the adsorbent.

These values are included in Table I and are of the same order of magnitude as those obtained by Bangham & Maggs for coal; no value for plaster obtained by mechanical means has been found for comparison, but these values are included here to show that by the use of compacts it is possible to obtain a value for Young's modulus that is of the same order of magnitude as for other materials.

By comparison of the surface areas of the samples obtained by the three different methods, it may be observed that, for pottery plaster, the results from the methanol and water isotherms agree quite closely, although they are only about one-third of the values obtained from the Kelvin equation calculation. It is concluded that the discontinuity is not the result of capillary condensation and thus a calculation based on the Kelvin equation is in error. For dehydrated precipitated gypsum the values from the water isotherm calculated by the B.E.T. method and the Kelvin equation agree closely, but the B.E.T. area calculations from the methanol and water isotherms differ greatly. As a result of these determinations of surface area by the B.E.T. method from the water sorption isotherm, it was possible to calculate the sorbed water at 5% humidity and to determine the expansion due to sorption at this humidity from the extrapolated curve AB. Thus, the curve for this humidity to zero for the sorption and expansion isotherms were drawn in as shown on Figs. 1 and 3—6, and it may be observed from the original curve that some hydration to hemihydrate still occurred at 5% humidity. It may also be observed that expansion due to hemihydrate formation is low; this agrees with observations of Bunn¹¹ that the dimensional change in the lattice due to hemihydrate formation is small.

The unusual form of the water sorption isotherms on the various types of plaster, in contrast with the methanol sorption isotherm, can be explained on the basis of the experimental work presented here. The discontinuity is not considered to be the result of capillary condensation or formation of subhydrate, but of activated adsorption.¹²

The existence of an intrinsic activation step in chemi-sorption is now well recognised and the magnitude of the energy barrier may vary considerably with the system concerned. It is a generally accepted hypothesis¹³ that the activation energy required to surmount the barrier between the approaching molecule and the surface is supplied entirely by the adsorbent. In this case, as the adsorbate goes on the surface, changes to the adsorbent occur. This can be well understood since the adsorbent is ionic in nature and by no means inert; there is considerable interaction between the adsorbent and adsorbate. In effect, an increase of the area available for adsorption is generated during coverage of the adsorbent by the adsorbate. Whether this is achieved by modification of the lattice spacing allowing greater penetration of the adsorbent, or by a change in interaction energies making more sites available for adsorption, is a matter of speculation. Thus, the characteristics of the isotherms on the different plaster samples will depend on their methods of preparation and will vary considerably with the adsorbate used. The fact that no comparable discontinuity occurred for the methanol isotherm at low pressures is probably due to the difference in the dipole moments per unit area of the methanol and water molecules, as it is to be expected that the interaction between adsorbate and adsorbent will influence the generation of further sites for adsorption.

This type of sorption cannot be of a reversible nature and the explanation of the discontinuity based on the above considerations would necessarily include an irreversible isotherm; this will account for the secondary hysteresis in these isotherms. An explanation for this secondary hysteresis has been attempted by Gregg & Willing;² isolated pockets of dihydrate are thought to exist, having been formed at higher humidities. X-ray diffraction work by the authors and others,¹ in which samples were exposed to various humidity conditions before final sealing in sample tubes, gives no evidence for this explanation.

If the calculation of the reduction of surface free energy lowering or of spreading pressure is carried out for relative pressures higher than 25—40% for different samples, the plot of $\Delta l/l$ vs ϕ (Fig. 8) yields a surprising increase in the slope of this curve immediately after the point equivalent to the discontinuities. For the sample of dehydrated precipitated gypsum the plot yields a straight line up to the point obtained at 60% humidity, after which a decrease in slope is observed. These plots can be understood if the discontinuity is considered to be the result of activated-adsorbed water. If new surface is made available spontaneously to an adsorbate at 25% relative vapour pressure, the amount adsorbed would be for the relative vapour pressure range from 0 to 25%. Thus, this adsorbate would not be desorbed at 25%, but would be in the range from 25 to 0%.

The calculation of the spreading pressure, by the Gibbs equation using the pressure at which the discontinuity occurred, would be in error. Since the discontinuity is extremely small for dehydrated precipitated gypsum, the plot of $\Delta l/l$ vs ϕ continues linearly up to a p/p_0 value of 0.60, after which presumably capillary condensation may commence. The history and method of the preparation of the sample must affect chemisorption on the surface, since differences are observed for the isotherms of the different types of plaster. It is known that, in the production of pottery plaster by the aridised process,¹⁴ large ordered crystals of hemihydrate are formed. The preparation of 'B-Base' hydrocal hemihydrate by the dehydration of gypsum in the presence of steam produces the largest and best ordered crystals of the four types of plaster.

This is well illustrated in the isotherm of the material and the very low surface area calculated from it. The precipitated gypsum samples, both the reagent grade and the 'Alba-Floc' dihydrate, have small crystals to start with, and dehydration to anhydrous calcium sulphate in vacuum would reduce further the size and order of the crystals. It may be expected that there will be differences in the state of these samples in comparison with the other two, and more active sites in the case of the dehydrated gypsum samples may already exist before sorption takes place.

Conclusion

By the use of compacts of powdered plaster of Paris, it has been possible to determine the dimensional changes associated with the sorption process on their surfaces. By application of the Gibbs adsorption equation to the sorption and dimensional change data and an assumption that for low coverages of sorbed water the $\Delta l/l$ vs ΔW plot is linear, a trial and error procedure was adopted from which quantities of sorbed and hemihydrate water were estimated. As a result, the surface areas of plaster samples, calculated by the B.E.T. method from the water sorption isotherm, were obtained. It was concluded from a comparison of this surface area and those obtained from other methods that the discontinuity observed at p/p_0 values of 0.25 to 0.40 was not from capillary condensation.

Further results from the dimensional change-spreading pressure plot and a secondary hysteresis observed in all the isotherms provided evidence that the discontinuity resulted from chemisorption on activated sites, generated during the process of adsorption.

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