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COMPACTS OF POWDERED MATERIAL AS POROUS BODIES
FOR USE IN SORPTION STUDIES

BY

P. J. SEREDA AND R. F. FELDMAN

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ANALYZED

COMPACTS OF POWDERED MATERIAL AS POROUS BODIES FOR USE IN SORPTION STUDIES

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

Details are given for the production of rigid porous bodies (compacts) made by compacting under high pressure fine powders in the particle range of $10-0.01\mu$ of silica, calcium carbonate, plaster of Paris and molecular sieves. These compacts were used as samples to study sorption and related dimensional changes. The results were used to compute spreading pressure by applying the Gibbs adsorption equation and allowed derivation of the $\Delta l/l$ vs ϕ plots using the Bangham relation.

With compacts made from molecular sieves, it was possible to study the forces imposed on the particles by water entering or leaving the micropore system.

Introduction

There has been a great need for rigid porous bodies that might be used to study the various phenomena, especially dimensional changes, associated with the sorption of water on internal surfaces of materials. Naturally occurring materials are usually non-homogeneous, non-isotropic and non-reproducible from sample to sample, and contain impurities in varying amounts. Of those synthetically produced, the two classical materials that have been used for such studies are carbon rods and Vycor glass, both of which represent an unusual range of porosity and internal surface area. To extend this range and to avoid some of the limitations of natural rigid porous materials, a technique has been developed to produce such porous bodies with a wider range of properties by compressing fine powders of different materials into compacts, as was done by Dollimore and co-workers,^{1, 2} and as is done in powder metallurgy and catalyst technology.

Powders of different materials in the particle range $10\text{--}0.01\mu$ were compressed in a mould at pressures of 4000 to 46,400 p.s.i. to give rigid porous bodies. Each powdered material has optimum conditions of moisture content and pressure at which satisfactory compacts are made. Although all finely powdered material will produce a rigid body when compressed at a suitable pressure, not all such compacts can withstand immersion in water without disintegration, nor do all have a sufficient mechanical strength when dry.

The formation of a rigid body by compression of a fine powder must involve, in the first place, the bringing together of enough of the surface at distances where the van der Waals' attractive forces come into play. As in the case of powder metallurgy, much strength of the compact can be derived from primary bonds resulting from bridging between particles in contact, where the surfaces are under pressure or are deformed and will recrystallise, hydrate or react more readily than other surfaces. Solid-state reactions can be postulated for the formation of bridges.³

Where the powder can hydrate, only traces of water may be required to cause bridging by the formation of minute quantities of the hydrate.

Experimental

Technique for preparation of compacts

For the work described in this paper, compacts measuring 3.125 cm. in dia. and about 1.5 mm. thick were made in a steel mould consisting of a cylinder and two closely fitting pistons. The cylinder was first mounted vertically, with the bottom piston located in the cylinder about 1.2 cm. below the top (this spacing varied for different powders and different compacting pressures in order to make the samples the same thickness). The powder was placed in the mould by tamping with the edge of a spatula against the top edge of the cylinder while excess powder remained heaped over the mould. Tamping with equally spaced strokes in two directions, at right angles to each other, was concluded by striking off the excess powder level with the top edge of the cylinder. The bottom piston was lowered with the sample and the top piston placed in the cylinder; the assembly was then mounted in a 60,000-lb. testing machine. While the first increment of load was applied, the cylinder was rotated slightly and held up to allow both pistons to float and to ensure that the compression of the sample was equal from both sides.

Pressures of 4000—46,400 p.s.i. have been used in compressing samples; when inert materials were used, a small amount of water was added to improve compression. All powders in the particle sizes 10μ and smaller had to be agglomerated by working them in a mortar with pestle (with or without the addition of water) until the powder formed coarse agglomerates, which could be packed more uniformly into the mould. This step proved important when compacting very fine powders such as silica (Cab-O-Sil), although in the case of plaster of Paris it was not necessary because the fine particles were already in a state of agglomeration. While some materials will form satisfactory compacts over a very wide range of pressures, others require a specific pressure to be satisfactory. If, after compression, the material tends to rebound or relax as if in a high state of strain, then the forming of a satisfactory compact above a certain pressure may be impossible; any density variation will result in cracking along lines of maximum density gradient representing different magnitudes of recovery or relaxation between two adjacent sections of the compact.

Procedure

Samples for determining both the sorption and expansion isotherms were obtained from the

same compact. Each compact was made in the form of a disc 1.5 mm thick and was cut to give two rectangular prisms 7×28 mm. to be mounted on extensometers, and two segments weighing about 1 g. to be mounted on the quartz spirals.

The apparatus consisted of six tubes mounting the McBain-Bakr type of quartz spirals, which were sensitive to 2.5×10^{-5} g. in conjunction with the cathetometer reading to 0.001 cm., and six cells equipped with optical windows containing the optical extensometers (modified Tuckerman gauge) sensitive to 2×10^{-6} in./in. The Tuckerman optical extensometer system was obtained from the American Instrument Co. The extensometer itself was modified to allow the mounting of the sample firmly on it and the prism was replaced by a polished metal mirror. These six cells were part of the high-vacuum system consisting of a three-stage oil diffusion pump backed by a rotary vacuum pump to obtain pressures less than 10^{-6} mm. Hg.

Water vapour or other adsorbates were introduced into the system from a bulb in a bath controlled to any desired temperature in the range -17 to 21° ($\pm 0.05^\circ$). The temperature of the samples was also controlled at 21° by means of a bath surrounding the tubes and cells.

Before determining the sorption and expansion isotherms, all samples were outgassed at 150 – 200° to a vacuum of less than 10^{-6} mm. Hg until negligible weight loss had been recorded for 15 h. For equilibrium to be attained between points along the isotherm, different periods were required for different samples. In all cases a period of about 15 h. of negligible weight change and negligible dimensional change was allowed before the system was considered to be in equilibrium.

Characteristics of compacts

Three types of systems were represented in the compacts produced for this study:

Type I: large particles having no internal micropores and low surface area. This system was represented by compacts of calcium carbonate of particle size about 1 – 5μ .

Type II: very small particles forming very small pores and giving a high surface area, represented by silica (Cab-O-Sil—supplied by Godfrey L. Cabot, Inc.) having particles 0.01 – 0.02μ .

Type III: large particles having an internal micropore system. In addition to giving a system such as Type I, it also gives a system such as Type II, of special character. Molecular sieves (Linde 4A—supplied by Linde Co.) having particles 2 – 5μ and micropores consisting of $11.4\text{\AA}$ cavities separated by $4.2\text{\AA}$ openings represented this system.

One of the most important properties of a compact to be used for studies such as those described here is the void fraction or porosity. It can be changed as much as two-fold by varying the pressure of forming for such materials as plaster of Paris (see Fig. 1). The void fraction was determined from measurements of the dimensions of the compact, the dry weight and the absolute density of the materials. In the case of mixtures of materials in one compact, it was difficult to determine the void fraction because the absolute density could not be known accurately. These data can also be plotted on the basis of axial stress as suggested by Amberg & Echigoya.⁴ This plot, however, does not give a common line for the different materials. Values for compacts of calcium carbonate and plaster of Paris do not fall on any of the plots given by Amberg & Echigoya.

It was considered of importance to determine the uniformity of the apparent density or porosity throughout the compact. To examine this property, compacts of different thicknesses were made at a series of constant pressure. Even though the thicknesses were varied tenfold there was no significant difference in the void fraction for plaster of Paris at several pressures, and similar results were indicated for other materials (see Fig. 2). From the work of Durvez & Zwell⁵ on metal powder compacts, it is evident that the pressure ratio should be very nearly unity for all sections of the compact, since all compacts, even the thickest used in this study, have a very low thickness-to-diameter ratio and are being compacted from both faces.

In the use of compacts for the study of the dimensional changes of materials during sorption of water, the important question to be answered is whether any strain remains in the compact as the result of compression of particles that may be relaxed during wetting, thus exhibiting a dimensional change in no way related to sorption of water on the surfaces. Compacts of some materials, such as plaster of Paris and calcium carbonate, will disintegrate when immersed in water, although they will not do so in kerosene or carbon tetrachloride. In fact, the dimensional change of these compacts during saturation from the dry state with these solvents is negligible. This would indicate that there is no residual strain in the compact.

Fig. 1. Effect of pressure on the void fraction of compacts

● calcium carbonate ○ pottery plaster □ molecular sieve Linde 4A

Fig. 2. Effect of thickness on the void fraction of compacts made at constant pressure

● pottery plaster compressed at 16,250 p.s.i.
 ▲ pottery plaster compressed at 8125 p.s.i.
 ○ calcium carbonate compressed at 8125 p.s.i.
 △ calcium carbonate compressed at 24,400 p.s.i.

That residual strain is absent is further supported by the results obtained by an application of the Gibbs adsorption equation. This equation relates the surface-free energy, lowering ΔF as sorption occurs on a surface, to the pressure p dynes/cm.² of the adsorbate, and the surface concentration s of the adsorbate on the adsorbent in g.-mol./cm.².

$$\Delta F = RT \int_0^p s/p \, dp$$

When ΔF ergs/cm.², commonly called ϕ , the spreading pressure, is calculated, a plot of $\Delta l/l$ vs ϕ should, according to the Bangham relation,⁶ $\Delta l/l = \lambda \Delta F$, 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.

This plot did, in fact, produce acceptable straight lines through the origin for the Cab-O-Sil and CaCO₃ samples in the region where adsorption without capillary condensation occurred. Similar plots for other materials, such as plaster of Paris, have been obtained and will be published separately.

Most compacts of different materials do show a relaxation in the high-humidity region or on saturation, represented by an irreversible portion of the expansion. This same phenomenon occurs with methanol, but to a lesser degree. To examine the extent of this irreversibility,

compacts were exposed to repeated cycles of wetting, either in saturated water vapour condition or by immersion, followed by drying over magnesium perchlorate or by vacuum to liquid air trap. Fig. 3 shows this tendency, which is especially pronounced where a large proportion of material like calcium carbonate was used; it is attributed to a rearrangement of some of the particles in the compact. Irreversible swelling of the compact on repeated cycling from the saturated to the dry condition is the manifestation of the loss of strength or deterioration of many materials when subjected to such cyclings. This relaxation or irreversible swelling phenomenon is of no concern in the region of relative humidity below the point where this is pronounced; for many materials this may be just short of saturation.

Fig. 3. Total expansion contraction during repeated cycling

△ water (compact 24,400 p.s.i.), 25% Cab-O-Sil, 75% calcium carbonate
 ○ water (compact 8125 p.s.i.), 50% Cab-O-Sil, 50% calcium carbonate
 ● methanol (compact 8125 p.s.i.), 50% Cab-O-Sil, 50% calcium carbonate
 (wetting by immersion and drying in vacuum)

Results

(1) Plaster compacts

Compacts have been prepared from several types of plaster of Paris and gypsum over a wide range of pressures (Fig. 1) to study the sorption-dimensional change relationship. Results of the study are reported separately. These compacts have also been used to study expansion during hydration at different temperatures; this is an extension of the work previously reported⁷ and will be published elsewhere.

(2) Calcium carbonate compacts

Compacts were formed from precipitated reagent-grade calcium carbonate at pressures of 8,000–46,400 p.s.i. The particles of powder were estimated to be about 2μ in diameter.

Figs. 4(a) and 4(b) show the sorption and expansion isotherms respectively for calcium carbonate compacts formed at 46,400 p.s.i. Both are Type II in Brunauer's classification, and the expansion isotherm shows a continual expansion for the extent of the isotherm. On desorption for the sorption isotherm, hysteresis is observed in the region of a p/p_0 value of 0.05–0.60. A value of 5.6 m.²/g. was obtained for the surface area by the B.E.T. method, and, because of this low value, high accuracy cannot be expected.

For the expansion isotherm, very little contraction was observed on desorption; apparently the sample had been exposed to humidities where rearrangement of the particles occurred. A plot of ΔW vs $\Delta l/l$ (Fig. 4c) illustrates this. The first portion of the plot, up to a p/p_0 value of 0.60 where sorption coverage is still low, can be considered linear through zero, as was observed by Amberg & MacIntosh⁸ for Vycor glass. A slight increase instead of decrease in slope was observed on approaching a humidity of 70%, before capillary condensation at 80–85% caused a decrease in slope. Fig. 5 illustrates this to advantage. The plot of $\Delta l/l$ vs ϕ produces a straight line up to a p/p_0 value of 0.60. Beyond this point an increase in slope may be observed, followed by a decrease after a p/p_0 value of 0.80. The explanation for this, as mentioned before, is the weakening of the bonds between particles and their subsequent rearrangement. Whether or not the mechanism of healing postulated by Dollimore & Gregg⁹ occurs at higher relative pressure was not studied. The decrease in slope at p/p_0 of 0.80 is due to the contractive force produced by capillary condensation. On desorption, this contractive force disappears and an even greater expansion of the sample takes place. A significant contraction occurs only at very low relative pressures.

Fig. 4. Results for calcium carbonate compact

(a) sorption isotherms (b) expansion isotherms (c) expansion as related to water sorbed

● adsorption ○ desorption

Fig. 5. Expansion of compacts as a function of the calculated spreading force

● calcium carbonate
○ 50% Cab-O-Sil + 50% calcium carbonate
△ 25% Cab-O-Sil + 50% calcium carbonate
(figures on curves are p/p_0 values)

By calculating the Young's modulus E for the material by a relation of Bangham from the $\Delta l/l$ vs ϕ plot

$$E = \rho A / \lambda$$

where ρ is the absolute density of the material (g./c.c.) and A the area (cm.²/g.), a value for E of 6.97×10^{10} dynes/cm² was obtained using a value of 2.93 g./c.c. for ρ . This value is within the same order of magnitude for materials of this nature.

Since compacts of calcium carbonate disintegrate on immersion in water it is not surprising that they show relaxation when a partial pressure of 0.6 is exceeded, this being in the region of multi-molecular sorption.

(3) Cab-O-Sil with admixture of calcium carbonate

Compacts of the pure Cab-O-Sil were too brittle to work with, and it was therefore diluted with various proportions of calcium carbonate. The 25% Cab-O-Sil compacts were made at a pressure of 46,400 p.s.i. and the 50% compacts at 24,400 p.s.i. Sorption and expansion isotherms are given for both of these compacts (Figs. 6 and 7).

Fig. 6. Results for compact of 50% Cab-O-Sil + 50% calcium carbonate

(a) sorption isotherms (b) expansion isotherms (c) expansion as related to water sorbed

● adsorption ○ desorption

Fig. 7. Results for compact of 25% Cab-O-Sil + 75% calcium carbonate

(a) sorption isotherms (b) expansion isotherms
(c) expansion as related to water sorbed

● adsorption

○ desorption

The adsorption isotherm for the 50% Cab-O-Sil/50% CaCO_3 compact (Fig. 6a) is a normal smooth Type-II isotherm. A B.E.T. calculation yields $36.1 \text{ m}^2/\text{g}$. for the surface area. The adsorption and desorption isotherms in the region of low p/p_0 values do not coincide and this separation is defined as secondary hysteresis. This is probably the result of the history of the preparation of the Cab-O-Sil silica and its resulting very small particle size.

The expansion isotherm (Fig. 6b) shows a flattening of the curve at a p/p_0 value of about 0.40 and a contraction continuing from 0.50 to the end of the isotherm. This effect is also exhibited in the desorption part of the cycle where first an expansion and then a contraction were observed. The effect of the secondary hysteresis manifests itself also in this plot.

The $\Delta l/l$ vs ΔW plot (Fig. 6c) shows, as it did in a similar plot for CaCO_3 , a linear portion for low coverages, in this case up to a p/p_0 value of approximately 0.35. A reduction of slope occurs at higher humidities until a contraction occurs after 0.50 p/p_0 . This contraction can be explained by the formation of menisci in this region; the contractive force due to menisci formation in the case of this material is greater than the expansive force due to the lowering of surface free energy. The fact that the desorption curve does not combine with the adsorption curve, but runs parallel to it, may be attributed to rearrangement at the higher humidities. The $\Delta l/l$ vs ϕ curve (Fig. 5) is a straight line through zero up to p/p_0 0.40, after which the slope is almost zero. This, together with the other plots, indicates that capillary condensation occurred for this compacted system in the region of p/p_0 values of 0.40–0.45. This represents an equivalent pore radius of 15.7 – $18.4 \text{ \AA}$. The value of E was calculated as $1.21 \times 10^{11} \text{ dynes/cm}^2$ using a density of 2.7 g./c.c.

In the sample with 25% of Cab-O-Sil and 75% of CaCO_3 , a similar result was obtained, although the effect of dilution of the Cab-O-Sil was noticed (Fig. 7). The area of the sample was $22.7 \text{ m}^2/\text{g}$. The contraction observed in the expansion isotherm was present, although it occurred at a later p/p_0 value than for the more concentrated Cab-O-Sil samples. Evidence that more rearrangement had taken place than for the previous samples was observed in the desorption parts of the $\Delta l/l$ vs ΔW plot, although the adsorption part of this curve was again linear for low coverages. The $\Delta l/l$ vs ϕ plot in this case did not give as acceptable a straight line as for the previous samples, the points for lower pressure deviating somewhat. The increasing dilution, the effect of which had been considered negligible, and the errors in the graphical integration may have caused this. The value for E , however, was calculated as $1.35 \times 10^{11} \text{ dynes/cm}^2$ (which is similar to the value obtained for those of higher concentrations). In this $\Delta l/l$ vs ϕ plot, the decrease in slope is again observed at p/p_0 values between 0.40 and 0.45, indicating, together with the other plots, capillary condensation at the same pressure as for the other samples.

(4) Molecular sieves with admixtures of calcium carbonate

Compacts of the zeolite molecular sieve (Linde 4A) formed at various pressures remained whole, even on immersion in water. In order to reduce the very large expansion on wetting, a calcium carbonate diluent was used. For this study all compacts containing this molecular sieve were made at a pressure of 46,400 p.s.i.

This unique material exhibited a specific sorption dimensional change relation consisting of a contraction on adsorption at relative pressures below 0.1 and even greater contraction during desorption as shown on $\Delta l/l$ vs ΔW plots (Fig. 8).

Fig. 8. Dimensional change as related to water sorbed for compacts of molecular sieves and calcium carbonate

25% molecular sieve + 75% calcium carbonate
 ● adsorption △ desorption
 75% molecular sieve + 25% calcium carbonate
 ○ adsorption ▲ desorption

Along the adsorption loop it is postulated that there is 'molecular bridging' in the 4.2Å openings; this type of bridging has originally been postulated by Lakhanpal & Flood¹⁰ for sorption on carbon. On the desorption cycle, however, the large hysteresis which cannot be explained by bridging, seems to suggest a tension in the water in the 11.2Å cavities. This tension is produced by the process of water molecules leaving the necks of the pores and being replaced by water molecules from the cavity. Since this contraction is occurring in the region of p/p_0 below 0.05, which represents an equivalent tension far in excess of what the column of water in the cavity can withstand, then the water is in a non-equilibrium state. The low rate by which it proceeds to equilibrium is governed by the rate at which water leaves the narrow necks of the molecular sieve and determines the extent of contraction. The contraction observed here is of the same order of magnitude as that observed by Wiig & Juhola¹¹ for water on activated charcoal.

As in previous cases where calcium carbonate was used, some relaxation at high relative pressures must have occurred; as the concentration of the molecular sieves was increased, there was a greater tendency for the desorption curve to pass through zero. In addition, the effect of dilution is manifested in the plot for the molecular sieve concentration of 25% where the contraction on adsorption observed for 75% was eliminated and the contraction on desorption was decreased.

Discussion and conclusions

It has been shown that compacts compressed from fine powders will behave as rigid porous bodies within certain ranges of partial pressures, and this enables the study of the sorption and the related dimensional changes of these materials. The fact that plots of $\Delta l/l$ vs ΔW and $\Delta l/l$ vs ϕ are linear over the useful range for compacts of these materials, as is the case for Vycor glass, confirms the validity of the above statement. The fact that samples of given materials can be made in a range of void ratios and in a range of surface areas makes these studies particularly significant. In a compact composed of very small particles, as in Cab-O-Sil, it was possible to observe formation of menisci and the resulting contraction during the adsorption part of the loop at relatively low p/p_0 values.

With compacts made from molecular sieves, it was possible to study the forces imposed on the particles by water entering or leaving the micropore system.

Relaxation of the compacts of some materials was observed at high humidities above the region where capillary condensation is expected to begin, thus limiting the useful range. Where hydrates are not involved, it should be possible to make compacts useful over the entire range of

relative pressures of water by following the procedures for sintering, as in the case of powder metallurgy and ceramics. Heating to temperatures of $0.5T_f$ (where T_f = melting temperature) should provide enough bridging between particles in close contact to prevent the relaxation that was observed in this study when certain partial pressure was exceeded.

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