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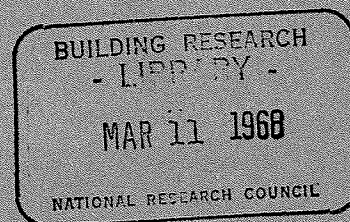
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LENGTH CHANGE CHARACTERISTICS OF $\text{Ca}(\text{OH})_2$ COMPACTS ON EXPOSURE TO WATER VAPOUR

By V. S. RAMACHANDRAN and R. F. FELDMAN

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**CARACTERISTIQUES DES MODIFICATIONS DIMENSIONNELLES
D'ECHANTILLONS COMPACTS DE Ca(OH)_2 EXPOSES A LA
VAPEUR D'EAU**

SOMMAIRE

La présence d'une forte proportion de Ca(OH)_2 dans les ciments Portland hydratés laisse supposer qu'une étude des rapports entre les modifications dimensionnelles d'échantillons de Ca(OH)_2 comprimés et leurs caractéristiques d'absorption donnerait des renseignements utiles.

Ces données ont été obtenues pour des degrés d'humidité relative allant de zéro à 76 pour cent; certaines expériences à variation cyclique du degré d'humidité relative de zéro à 58 et à 93 pour cent ont également fourni des données sur le rapport mentionné ci-dessus. Les auteurs ont aussi entrepris des expériences préliminaires sur la carbonatation des échantillons de Ca(OH)_2 comprimés.

Ils ont observé d'importantes contractions irréversibles au cours du traitement à humidité constante et du traitement à variation cyclique du degré d'humidité, et en ont conclu qu'elles résultaient de la diffusion des ions à partir des points de contact des cristallites et de l'agglomération de ces dernières par les forces de Van der Waals.

La carbonatation de la chaux hydratée produit également des contractions. Les auteurs considèrent que les forces superficielles de Van der Waals en sont largement responsables.



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LENGTH CHANGE CHARACTERISTICS OF $\text{Ca}(\text{OH})_2$ COMPACTS ON EXPOSURE TO WATER VAPOUR

By V. S. RAMACHANDRAN* and R. F. FELDMAN

The presence of large quantities of $\text{Ca}(\text{OH})_2$ in hydrated Portland cement suggests that a study of the length change-sorption characteristics of $\text{Ca}(\text{OH})_2$ in the form of compacts should provide useful information.

Length change-sorption data were obtained for water from 0 to 76% RH and various cycling experiments between 0 to 58 and 0 to 93% RH were performed during which length change data were obtained. Preliminary experiments were also performed in relation to the carbonatation of $\text{Ca}(\text{OH})_2$ compacts.

Large irreversible shrinkages were observed while repeatedly determining the isotherms during the cycling experiments and it is suggested that these were the result of ionic diffusion from the points of contact of crystallites and the pulling together of these crystallites by van der Waals forces.

The carbonatation of calcium hydroxide also produced shrinkage and it is considered that this could also be due to van der Waals surface forces.

Introduction

Sorption isotherms for a variety of porous materials have yielded a great deal of information about their physical state.¹ Length change isotherms obtained at the same time as the sorption isotherms have been used to provide much additional information concerning the interaction between adsorbent and adsorbate.²

$\text{Ca}(\text{OH})_2$ is present in large quantities in hydrated Portland cement, and thus its water sorption and length change characteristics and their irreversibility are of great importance. Further work has been done in the Division of Building Research on mechanical properties and carbonatation of $\text{Ca}(\text{OH})_2$.

Sorption isotherms by Glasson³ exhibited an unexplained secondary hysteresis, and it is considered here that this phenomenon is related to the ageing and shrinking properties of $\text{Ca}(\text{OH})_2$. The carbonatation shrinkage observed in Portland cement⁴ has been related to its $\text{Ca}(\text{OH})_2$ content and this is also discussed in relation to the dimensional stability of the $\text{Ca}(\text{OH})_2$ compact.

In this work, length change-sorption results were obtained for water from 0 to 76% RH; various cycling experiments between 0 to 58 and 0 to 93% RH were performed during which length change data were obtained. Preliminary experiments were also performed on the carbonatation of $\text{Ca}(\text{OH})_2$ compacts.

Experimental

Reagent grade $\text{Ca}(\text{OH})_2$ of the following composition, $\text{Ca}(\text{OH})_2$ 97.7; CaCO_3 0.58; SiO_2 0.38; Al_2O_3 0.05; Fe_2O_3 0.05; MgO 0.49; CaSO_4 0.15 and sulphur 0.035% was used to make the samples and compacts for these experiments.

The procedure for making the compacts and the samples has been described previously.⁵ Compacts were formed at a load of 20,000 lb in a mould of 1.25 in. diameter. Work has shown that compacts can be made reproducibly, and that, because they are no more than $\frac{1}{16}$ in. thick, they attain equilibrium quickly.

A high-vacuum apparatus (min. pressure 10^{-6} mm Hg) was used in this work. The samples were mounted on quartz spirals of the McBain-Bakr type and gave values of weight changes to a sensitivity of 2.6×10^{-5} g. For dimensional change measurements, samples were mounted on modified Tuckerman optical extensometers and placed in cells equipped with optical windows. The dimensional changes could be determined with a sensitivity of 4×10^{-6} in./in.

Similar compacts mounted on extensometers were used in the carbonatation experiments. They were exposed to 50% RH in a vacuum cell for 24 h; the humidity condition was controlled by a sulphuric acid solution. The cell was then filled with CO_2 and joined to a large balloon also filled with CO_2 . The sample was thus exposed to CO_2 at approximately atmospheric pressure and to 50% RH. Measurements

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of length change were made as a function of time for approximately two weeks, the degree of carbonation being determined by thermogravimetric analysis after that period.

Samples measuring approx. $1\frac{1}{8}$ in. \times $\frac{3}{8}$ in. \times $\frac{1}{16}$ in. were cut from the compact and mounted, one on the extensometer and the other on the quartz spiral. Degassing of the samples was achieved by pumping with a rotary pump through a liquid air trap for 1 to 3 days.

The control of the vapour pressure in the apparatus at any desired level was achieved by the regulation of the temperature of the water source. The water source was contained in a bulb connected to the apparatus and immersed in a temperature controlled bath.

Samples were exposed for one to two days to a constant vapour pressure for each point along the isotherm.

Results

The water sorption isotherm for the $\text{Ca}(\text{OH})_2$ compacts is shown in Fig. 1. It is a normal Type II isotherm. Calculation according to the method of Brunauer, Emmett & Teller¹ gave a value of $13.2 \text{ m}^2/\text{g}$ for the surface area. The desorption isotherm, also shown in Fig. 1 was not obtained in detail but it is clear that a secondary hysteresis exists (i.e. the adsorption and desorption isotherms in the region of low relative pressure, p/p_0 , do not coincide). This secondary hysteresis has been well established for $\text{Ca}(\text{OH})_2$ by Glasson.³ The primary hysteresis extends at least to p/p_0 0.37, which is rather low, but this may be associated with the secondary hysteresis effect and not, as is usually assumed,¹ due to small pores.

The length change isotherm shown in Fig. 2, curve (I), was obtained from 0 to 74% RH. The plot of $\Delta l/l$ (relative length change) vs. $\Delta W/W$ (relative weight change) is shown in Fig. 3. The latter plot is linear from zero to about p/p_0 0.35; a decrease in slope occurs at higher humidities; at p/p_0 0.35, 1 to 2 molecular layers are adsorbed. This linear plot was also observed for the adsorption of water on porous glass,⁶ 'Cab-O-Sil' silica,⁵ precipitated calcium carbonate,⁵ calcium sulphate hemihydrate,⁷ and hydrated Portland cement.^{8,9} This is taken to indicate that the length change up to p/p_0 0.35 in the system of $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ is due largely to physical adsorption.

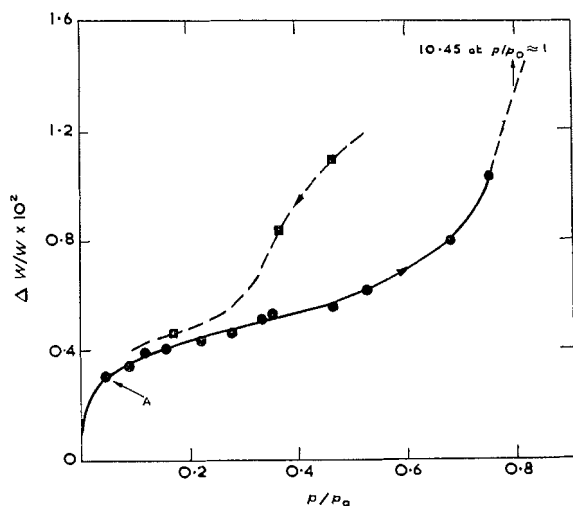


Fig. 1. Sorption isotherm of water on $\text{Ca}(\text{OH})_2$

● — adsorption ■ — desorption

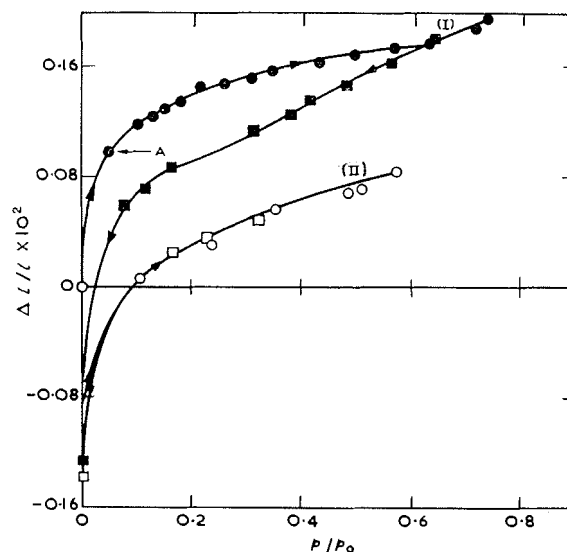


Fig. 2. Length change isotherms for first cycle (I) and second cycle (II)

● — adsorption ■ — desorption
○ — " □ — "

A plot of ΔF , the spreading pressure, or surface energy decrease due to physical adsorption against $\Delta l/l$ is shown in Fig. 4. The values of ΔF and $\Delta l/l$ at p/p_0 0.05 were taken as reference for the calculation; this was to avoid the difficulty in integrating sorption curves to zero. ΔF was calculated from the Gibbs adsorption equation:

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

This equation relates ΔF to the pressure p dyne/cm² of the adsorbate, and the surface concentration of the adsorbate

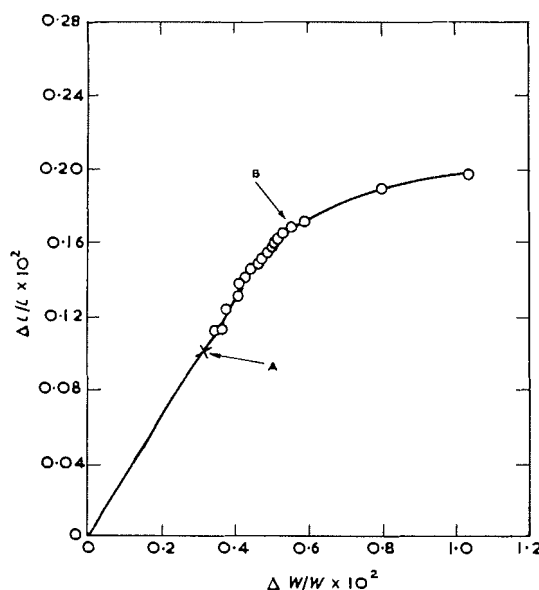


Fig. 3. Variation of relative length change ($\Delta l/l$) with relative weight change ($\Delta W/W$)

Point A calculated by method of Brunauer, Emmett & Teller¹
Point B $p/p_0 = 0.45$

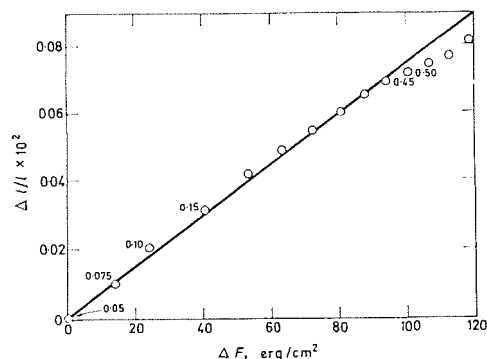


Fig. 4. Variation of relative length change ($\Delta l/l$) with surface energy decrease (ΔF)

Values of p/p_0 are indicated on the curve

on the adsorbent in gmol/cm^2 . The plot in Fig. 4 yields a straight line up to p/p_0 0.40 thus obeying the Bangham relation, $\Delta l/l = \lambda \Delta F$. λ is a constant related to the elastic coefficient of the material. The results deviated from the linear plot at p/p_0 values higher than 0.40, and indicated that some process was occurring that caused a decrease in the expansion for a given ΔF calculated on the assumption of physical adsorption. This will be discussed later. The linear $\Delta l/l$ vs. ΔF plot is taken as further evidence that the sorption length change process from p/p_0 0.05 up to approximately 0.40 was essentially the result of physical adsorption.

It is possible to calculate Young's modulus for the $\text{Ca}(\text{OH})_2$ from the $\Delta l/l$ vs. ΔF plot. Assuming an infinitely long cylinder, where the surface area is taken to be composed only of the curved surface of the cylinder, Bangham & Maggs¹⁰ derived the relation: $E = \rho\sigma/\lambda$, where E is the Young's modulus of the solid material, ρ the density (g/cc), σ the surface area (cm^2/g). A value of E for $\text{Ca}(\text{OH})_2$ from this equation will be in error owing to an incorrect geometric representation and to the fact that $\Delta l/l$ measured from an aggregate of $\text{Ca}(\text{OH})_2$ crystals of large porosity will not transmit the $\Delta l/l$ of each effectively through the body. The value, however, for $\text{Ca}(\text{OH})_2$ falls within those calculated for other materials (Table I) from sorption measurements; the value actually measured for the $\text{Ca}(\text{OH})_2$ compact by mechanical means is very similar to the calculated value, but it has a porosity of 33% by volume, so that the measured value would be considerably greater at zero porosity. It is pertinent that values are at least of the same order of magnitude.

The desorption part of the loop on the length change isotherm shows an unusually large contraction from p/p_0 0.63 downwards. At p/p_0 0.73, only 2 to 3 molecular layers exist and large hysteresis effects are not expected. At lower values

of p/p_0 , below 0.15, this shrinkage is very large and a large irreversible effect is observed. A net shrinkage of 0.126% from the original zero is observed. It is considered that the contraction starting below p/p_0 0.63 is the beginning of the large irreversible contraction observed below a p/p_0 of 0.07.

Curve (II) in Fig. 2 shows the second adsorption-desorption cycle, up to p/p_0 0.575. The adsorption part of curve (II) is very similar to that of curve (I) except that it is displaced by the large irreversible contraction that took place during the cycling curve (I). Unlike curve (I), the adsorption-desorption curves for curve (II) are close together, but there is a further irreversible shrinkage, zero now being at $\Delta l/l = -0.138 \times 10^{-2}$. Cycles (III) to (VI) are shown on Fig. 5, curves III to VI, respectively. Cycle (III) is for p/p_0 0.81, an irreversible shrinkage taking place at the lower humidities takes the zero to -0.186×10^{-2} , and cycle (IV) for p/p_0 of 0.83 produces a further irreversible shrinkage to -0.224×10^{-2} . Cycle (V) for p/p_0 0.93 shows an irreversible expansion both at higher humidities (compare p/p_0 of 0.15 on desorption with curve (IV)) and at zero which is -0.144×10^{-2} . Cycle (VI) for p/p_0 0.78 again yields an irreversible shrinkage, some of this taking place at humidities above p/p_0 0.10, the zero attaining a value -0.174×10^{-2} . Thus, on repeated cycling of a sample, maximum irreversible shrinkage takes place on

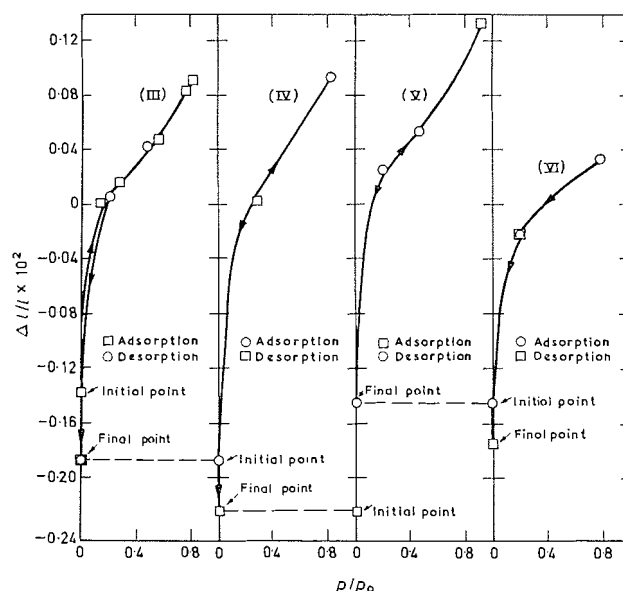


Fig. 5. Length change measurements associated with sorption of water on $\text{Ca}(\text{OH})_2$

(III) third cycle, (IV) fourth cycle, (V) fifth cycle, (VI) sixth cycle

TABLE I
Comparison of Young's modulus (E) for various materials

Material and state	E measured by mechanical means, dyne/cm^2	E calculated from sorption measurements, dyne/cm^2
Calcium sulphate hemihydrate (compact)	—	$0.106-0.587 \times 10^{11}$
Calcium hydroxide (compact)	$0.35-0.48 \times 10^{11}$	0.392×10^{11}
Calcium carbonate (compact)	—	0.697×10^{11}
Hydrated Portland cement (compact)	$0.87-2.8 \times 10^{11}$	0.973×10^{11}
'Cab-O-Sil' (finely divided) silica (compact)	—	1.21×10^{11}
Porous glass	$5.90-7.8 \times 10^{11}$	3.8×10^{11}

cycling up to p/p_0 0.73–0.83. After samples are cycled to higher values some of the irreversible shrinkage may be lost and after cycling up to values in the order of 0.50 further shrinkage may be relatively small. The sequence of cycling is important; irreversible shrinkage for any condition will be a maximum on the first cycle after sample preparation.

The results for the carbonatation of the $\text{Ca}(\text{OH})_2$ compact are shown on Fig. 6. Shrinkage occurred rapidly up to 45 hours, and a total shrinkage of 0.246% was recorded after 270 hours. The degree of carbonatation was 52%.

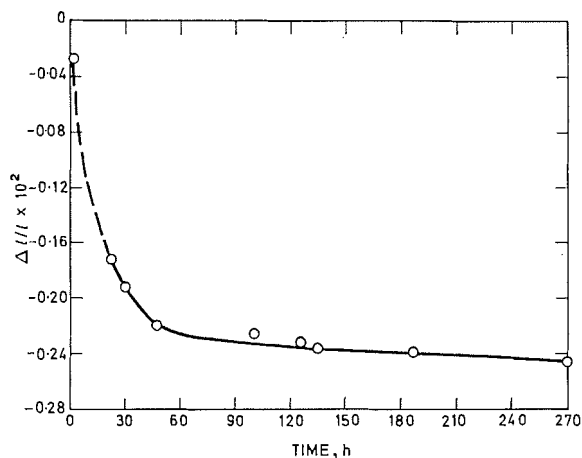


Fig. 6. Shrinkage of $\text{Ca}(\text{OH})_2$ due to reaction with CO_2

Discussion

The results have shown that the length change-sorption characteristics of the $\text{Ca}(\text{OH})_2$ compacts for relative vapour pressures below 0.40 are consistent with those obtained for other materials,⁵⁻⁹ most of which are relatively inert to water vapour.

The behaviour of $\text{Ca}(\text{OH})_2$ at higher relative vapour pressures is unique and it is suggested that ionic diffusion and movement into spaces vacated by the solid through this diffusion are the possible mechanisms leading to the observed irreversible shrinkage.

The points of contact of crystallites, as discussed by Rehinder & Segalova,¹¹ are thermodynamically in an unfavoured state due to their small size and high strain. Since $\text{Ca}(\text{OH})_2$ is water soluble, it is not unreasonable to expect these points to dissolve and diffuse away to crystallise at other sites in the porous solid. One would expect this diffusion process to depend on the concentration of adsorbed water on the $\text{Ca}(\text{OH})_2$ surface and time; greater adsorption occurs at higher relative pressures presumably allowing the diffusion process to occur. At relative vapour pressures below 0.40, results showed that the length change is due essentially to physical adsorption, indicating that insufficient water molecules are present for a very extensive diffusional process to take place in a short period of time.

Although a mechanism for the creation of spaces between crystallites, consistent with the experimental observations, has been proposed, it still remains to describe the force by which the crystallites are pulled together. One such force, the force due to the menisci of the water condensed in the small pores of an adsorbent has been shown to cause compressive stresses within a material.⁶ However, these stresses occur on the desorption part of the primary hysteresis loop

and at somewhat high relative vapour pressures, while it was observed (curve I) Fig. 2) that the large shrinkages took place below a relative vapour pressure of 0.63, with the greater part occurring below a relative vapour pressure of 0.08. The van der Waals forces from a surface that result in the physical adsorption of gases will also result in an attractive force between surfaces, the force depending on the distance separating the surfaces and degree of adsorption on the surface. The van der Waals force between crystallites is proposed as the main mechanism by which the shrinkage process occurs, causing the crystallites to move together into the holes made by the diffusion process; the menisci force may have a role at higher relative vapour pressures.

The van der Waals force mechanism would lead one to expect a lower attractive force between crystallites at the higher relative vapour pressures since this force will be decreased by the presence of water molecules in the spaces between the crystallites; when the relative pressure is lowered, as was done in the cycling experiments, a reduction in the sorbed water will increase the attractive force between crystallites. This may lead to the large shrinkages that were observed if enough spaces have been formed by ionic diffusion; if some of the spaces are too large, the attractive force between these crystallites may be too weak to contribute to the shrinkage force; the latter may explain the reduction in shrinkage when the $\text{Ca}(\text{OH})_2$ was exposed to a relative pressure of 0.93; here, a rapid diffusional process may have occurred with the larger quantity of adsorbed water and some of the vacated spaces may have become too large.

If the crystallites have come close together under conditions of low relative vapour pressures (less than 0.05), one would expect the van der Waals force between them to be large, and re-adsorption to a relative vapour pressure of approximately 0.40 will not be accompanied by their re-separation. The results on Fig. 2, cycle II, support this view.

These processes can account for the unexplained secondary hysteresis observed by Glasston³ for the water sorption isotherm of $\text{Ca}(\text{OH})_2$ which cannot be explained by an increase in surface area during the sorption cycle since Glasston found that the area had not changed significantly. During both the processes of diffusion and recrystallisation and of the meeting together of crystallite surfaces, adsorbed water could become trapped within spaces, and only 'hard drying' would remove this water, thus accounting for the secondary hysteresis. The secondary hysteresis is taken to indicate that processes of the nature discussed above are occurring. The fact that there is little change in surface area is illustrated by the similarity of the adsorption curves (I) and (II) of Fig. 2.

The large shrinkage of the calcium hydroxide compact in its reaction with CO_2 as shown on Fig. 6, leads one to speculate that the shrinkages observed in the sorption and carbonatation experiments are of similar origin. In this case, however, the presence of CO_2 accelerates the first process (the removal of the material by diffusion), perhaps in the form of the soluble calcium bicarbonate, creating vacant sites, which are pulled together by surface forces as in the case of $\text{Ca}(\text{OH})_2$ above. In a theory of carbonatation of Portland cement⁴ it was found necessary to postulate the existence of menisci to provide the force for shrinkage. It is shown in this work that van der Waals surface forces can also provide a mechanism for the shrinkage force in carbonatation of $\text{Ca}(\text{OH})_2$. Further work is needed to clarify the mechanism of the carbonatation process.

Conclusions

Adsorption-length change characteristics of the $\text{Ca}(\text{OH})_2$ compact up to relative pressures of water vapour of 0.40 are similar to those of relatively inert adsorbents; they are explained by the reduction of surface free energy and obey the Gibb's adsorption and Bangham equations.

A hypothesis for the irreversible shrinkage observed during water sorption-desorption cycles is given, namely, that the points of contact of crystallites are dissolved away by ionic diffusion in the sorbed water and the crystallites are pulled together into the holes by van der Waals forces, the trapping

of water in pockets thus created causing the secondary hysteresis observed in $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ isotherms, by the processes described above.

The carbonatation of calcium hydroxide shows a shrinkage similar to that previously observed for hydrated Portland cement.

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