

# ASSESSMENT OF EXPERIMENTAL EVIDENCE FOR MODELS OF HYDRATED PORTLAND CEMENT

R. F. Feldman, Division of Building Research, National Research Council of Canada,  
Ottawa

The relative merits of the "new" and "old" models of hydrated portland cement are presented together with an assessment of published and some unpublished evidence relating to the models. The chief areas of evidence discussed are those pertaining to surface energy of calcium-silicate-hydrate material (C-S-H) by heat of solution, stoichiometry of C-S-H, and the effect of interlayer rehydration of D-dried C-S-H on density measurements, c-axis and hydrated radii calculations, length and weight change isotherms, and porosity and mechanical property correlations. A new technique of measuring the flow rate of helium into interlayer spaces is discussed in terms of evidence it produces. It is concluded that the "new" model of hydrated portland cement more accurately accounts for its nature as indicated by a wide variety of properties.

•THERE ARE many terms used throughout this discussion to describe elements and conditions of hydrated portland cement. These are defined in the following:

1. C-S-H is the poorly crystallized, layered calcium-silicate-hydrate material found in well-hydrated portland cement,  $C_3S$  and  $C_2S$ .
2. A layer is the basic unit of the C-S-H structure; it is about 9 Å thick in the c-direction. This term is used synonymously with sheet.
3. Interlayer space is the space between layers, when essentially parallel, separated by no more than about 5 Å. Disorientation of layers may lead to greater distances in local areas.
4. Interlayer water occupies space between adjacent layers of C-S-H and is less mobile than free or physically adsorbed water.
5. Physically adsorbed water is water that is held to an open surface and that has energies not much more than the latent heat of evaporation. It does not have a role in the structure, nor does it contribute to the mechanical properties of the material. As defined here, it does not include interlayer water.
6. Nitrogen area is the surface area calculated from nitrogen adsorption results. It does not include the area between adjacent C-S-H layers.
7. Water area is the surface area calculated from water sorption results. The physical significance is difficult to specify because interlayer water appears to reenter interlayer space in an unpredictable way throughout the BET region normally used for surface area calculations.
8. Solid volume is the volume of the C-S-H layers, the volume of the interlayer water, and the unoccupied interlayer space.

9. The D-dried condition is the condition in which a sample has been dried to equilibrium at the water-vapor pressure of  $5 \times 10^{-4}$  mm of mercury.

10. The P-dried condition also involves drying but at a pressure of  $8.15 \times 10^{-3}$  mm of mercury.

11. Density is of 3 types: (a) density of undried material at 11 percent relative humidity (RH) that includes the interlayer water and interlayer space as solid volume in the calculation (physically adsorbed water is not counted as solid volume); (b) density of D-dried material that does not include the partially collapsed interlayer spaces as solid volume in the calculation (an approximation of this value is obtained by using water as the medium in the determination); and (c) density of D-dried material that includes the partially collapsed interlayer spaces as solid volume in the calculation.

Scientific interest in the experiments that provide evidence for a model for hydrated portland cement paste is currently at a high level. A new model subsequently called the F-S model (Feldman-Sereda model) has recently been proposed (1) that has given rise to extensive discussions (2, 3) comparing it with earlier ones.

The F-S model of hydrated portland cement is based ultimately on 3 fundamental assumptions (considered here as established facts) concerning the nature of the hydrated calcium silicates (assumed to be layered) normally found in hydrated portland cement. These assumptions are as follows:

1. The fundamental physical properties, such as density, equivalent c-spacing, Ca-Si ratio,  $H_2O$ -Si ratio, of hydrated portland cement or of the hydrated silicates and surface area vary with conditions of preparation. These conditions include water-solid ratio, temperature, and perhaps the content of alkali, sulfate, and admixtures.

2. When the hydrated material is D-dried, interlayer water is removed from the silicates. When it is reexposed to water vapor, water reenters the interlayer spaces even at low humidities.

3. In light of this conclusion, water surface areas and densities are therefore not correct, but the respective measurements by nitrogen and methanol are approximately correct.

These assumptions were considered wholly or partly incorrect in 1958 (4), even though surface areas determined by nitrogen before that date were given some credence by Kalousek (5) and Brunauer, Copeland, and Bragg (6). The basis of the old model, subsequently called the B-P model (Brunauer-Powers model), was that these assumptions were essentially incorrect, and a great deal of effort was spent in attempting to correlate and understand new data. As more and more data were accumulated, the assumptions had to be reevaluated. In 1964, Feldman and Sereda (7) suggested that assumptions 2 and 3 were true. In 1968 they described the F-S model (1), which is based on data from a variety of measurements on both compact and paste samples. These data included sorption, length change (8), strength, and other mechanical measurements (9), as well as surface area, chemical, and mineralogical considerations.

Other authors have also raised questions about aspects of the B-P model. Taylor (10) has expressed doubt about the supposed similarity of the hydrated silicates to the tobermorites and thus about the relevancy of the term "tobermorite gel"; hence, his preference for the nomenclature C-S-H. He considered the silicates to be very variable in composition and very heterogeneous. He has also questioned the very high density values used by Brunauer, Kantro, and Copeland (4) for a c-axis calculation. Locher (11) and Kurczyk and Schwiete (12) have questioned assumptions and methods used in the Ca-Si ratio determinations and results that show that the Ca-Si ratio varies inversely with the water-cement ratio (13). Seligmann (14) has analyzed nuclear magnetic reso-

nance measurements that he and others obtained and concluded that a large portion of what was considered as physically adsorbed water is interlayer water. Verbeck and Helmuth (15) have gone further and have concluded that the water formerly considered as gel water is interlayer water and that gel pores are, in fact, interlayer spaces. These conclusions all fit in with the descriptions and predictions of the F-S model.

There still remain, however, several areas of experimental evidence that are considered to cast doubt on the F-S model (2). These will be discussed in the following sections, and a considerable amount of new experimental evidence will be introduced. It is believed that the analysis of all the results makes the case for the F-S model convincing and provides the basis for a revision of the stoichiometry and "average interlayer spacing" of C-S-H gel.

#### SURFACE ENERGY OF C-S-H BY HEAT OF SOLUTION

The greatest difference between the F-S and B-P models of hydrated portland cement arises from assumptions 2 and 3 given earlier. The measurement of the surface energy of C-S-H gel by the heat-of-solution technique (16) has been considered by some (2) to be the strongest supporting evidence for the B-P model. It has been claimed that this measurement indicates that the surface area is correct when determined by water adsorption and is incorrect when determined by nitrogen adsorption. The following points indicate that this claim is doubtful:

1. Consideration of the surface energy of a material must include an assessment of the nature of the material and the type of surface involved. C-S-H is considered to be a layered crystal, the thickness of each layer being about 9 Å. Surface energy is the excess energy between the surface and the bulk. One is, therefore, immediately confronted with the difficult task of establishing whether the term "surface energy" has any meaning in layered materials; i.e., there is no real "bulk state."

2. As in the case with many clays of a layered nature, such as montmorillonite, C-S-H hydrates have both an internal and external surface. Nitrogen surface areas yield the external surface. If the unit cell structure or surface area per layer as proposed by Brunauer, Kantro, and Copeland (4) is correct, the internal plus the external surfaces are approximately 755 m<sup>2</sup>/g; thus, without even considering the dubiousness of the concept of surface energy as considered in point 1, one evidently cannot use water areas or nitrogen areas for computing correct overall surface energies.

3. The discussion in point 2 shows that it was erroneous to reason (2) that surface energies, based on nitrogen areas, give values that are too high or too low (negative). In fact, if 755 m<sup>2</sup>/g were used as a total area, a value closer to that of amorphous silica (16) would be expected. This emphasizes the irrelevance of the geometric mean of the surface energies of Ca(OH)<sub>2</sub> and amorphous silica that has been quoted by some workers (16). It can be questioned why these workers selected the values of crystalline Ca(OH)<sub>2</sub> and amorphous silica (2) for this calculation of surface energy because the Ca(OH)<sub>2</sub> in C-S-H is not crystalline.

4. The determination of specific surface energy by the heat of solution method is based on a very important assumption: The materials being studied are alike in every way except for their surface areas. Unfortunately, because the C-S-H materials were prepared by different methods, the materials would not be alike, as was pointed out earlier in assumption 1. To start with, the Ca-Si ratio of the C-S-H is now known (13) to vary inversely with the water-cement ratio for normal paste hydrated samples. This leaves several possibilities: (a) If the change in Ca-Si ratio is due only to additional Ca<sup>++</sup> deposited between the layers (in an unknown state), then the internal surface energy can be changed because the surfaces are different with different amounts of

$\text{Ca}^{++}$  and because the separation of the layers will vary. Evidence for the last statement has been obtained and will be discussed later (see section on density measurements and C-spacing). (b) The change in Ca-Si ratio might also be due either to silicone being substituted by calcium within the layer or to a different degree of silica condensation that, as has been shown by Lentz (17), occurs continuously. Owing to the diverse methods of preparing and starting materials, there is a clear possibility that the degree of polymerization of silica varies from preparation to preparation. In other words, variation in body structure and, therefore, body energy is a distinct possibility.

5. An evaluation of a paper by Brunauer, Kantro, and Wiese (16) on surface energy measurements on C-S-H gel led to the following observations: (a) The heat of solution for all their samples varied between 473 and 487 cal/g, a difference of 14 cal/g; for 2 identical samples, the difference was about 3.75 cal/g. It must be concluded that the precision of the data is not enough to make far-reaching conclusions. (b) The data fell into 3 clusters. Each cluster was almost completely composed of samples prepared by the same method: either the ball-mill, the paste, or the bottle-hydrated method. Within each cluster the results were scattered and, in some instances, negative surface energies could be calculated from the data when plotted against the water surface area. (c) Brunauer, Kantro, and Wiese (16) cited 2 samples, D-28 and D-35, when they discussed computation of surface energy. They suggested that if the surface areas of the samples as determined by nitrogen adsorption were used a negative surface energy would result. These samples, however, were made not only from different groups with regard to preparation but also from different materials. Sample D-28 was prepared by ball-milling  $\beta\text{-C}_2\text{S}$  for 46 days; D-35 was prepared by bottle-hydrating  $\text{C}_3\text{S}$  for 47 days. If one plots the nitrogen area for a group and makes comparisons for the same starting material, negative energies are not obtained. The data for nitrogen area, however, are very sparse.

6. A subsequent paper by Kantro, Wiese, and Brunauer (18), which contained heat of solution data, attempted to correct empirically for variation of Ca-Si ratio and water content. The application of regression analysis here raises the question, Did the variation in Ca-Si ratio cause the observed change in heat of solution, or did it change something else that in turn caused the change? The change in Ca-Si ratio most probably changed the nature of the surface as well as the surface area, body energy, and total heat of solution.

Kantro, Wiese, and Brunauer (18) attempted a difficult task with many inherent complications. It appears, however, that the ideas behind this work were based on the early concept of the nature of C-S-H (see 3 assumptions in first part of paper). With the present knowledge (assumption 1), which Kantro, Wiese, and Brunauer helped in a large measure to accumulate, it is clear that the heat of solution measurements should be reevaluated.

## INTERLAYER WATER AND RELATED PROBLEMS

### Density Measurements

Assumption 2 presents an important concept concerning interlayer water reentering D-dried material. The significance of this concept has been emphasized in the literature (2), and important questions concerning surface-area determinations by water and density determinations by lime-saturated solutions have been raised. If interlayer water reenters the structure—and several researchers (14, 15, 19) now believe that this is what happens—measured densities obtained by pycnometric techniques would approach that of the individual layers, if the value of the density of interlayer water is known and included in the calculation. It has been assumed, however, that

the layers completely collapse on D-drying, but this does not occur (20, 21). This incorrect assumption will lead to errors in estimates of a *c*-spacing or density and of a *c*-spacing of higher hydrates (e.g., P-dried specimens). The interlayer space is normally occupied by the maximum amount of hydrate water under normal conditions of concrete use, and so porosity or density calculations with the space included as solid matter are most relevant. This point will be discussed in detail in a later section.

In an experiment by Brunauer, Kantro, and Copeland (4), the weighed D-dried sample was soaked in a bottle or similar arrangement until the liquid was eventually brought to a certain level, after which the container was weighed. By this time the interlayer water would already have reentered the sample, with the result that the solid volume would appear low and the density too high; this is precisely what resulted (4). If the interlayer water had reentered very slowly subsequent to the measurements, a gradual increase in apparent density for both completely or partially dried samples would have resulted. Some authors, however, reported a gradual decrease in density when measurements were made in this way on partially dried samples, and they explained it by assuming gradual interlayer penetration (4). Some other explanation will have to be found; progressive changing in the state and position of  $\text{Ca}^{++}$  ions between the layers is perhaps a solution.

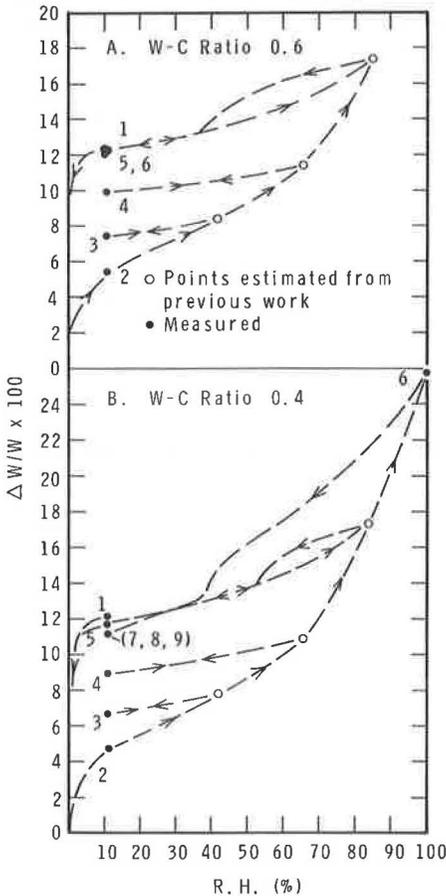


Figure 1. Isotherms for hydrated portland cement pastes.

This author is not aware of any evidence that shows that water cannot reenter the spaces between the C-S-H layers. In fact, much evidence exists to the contrary. Figure 1 shows recent work by this author on 0.6 and 0.4 water-cement ratio pastes hydrated for 2.5 years. These samples were stored for more than 2 and 4 months respectively at 11 percent RH, were then dried in stages well beyond the D-dried position during a period of 40 days, and were finally heated under vacuum to 190 C. They were then exposed to various humidities but always taken back to 11 percent RH before being advanced to a higher humidity.

The dashed lines shown in Figure 1 illustrate the significance of returning to 11 percent RH and how these paths are reversible (8). In an ideal adsorption system, all the numbered points at 11 percent RH should be identical, but in this case the position changes with each further advance of humidity. (An ideal adsorption system is one in which the system can be uniquely defined by temperature and relative pressure for constant surface area and other adsorbent properties in all but the primary hysteresis region. This region rarely exists below 35 percent RH and 11 percent RH should uniquely define such a system.) Previous work (8) has shown that this phenomenon is related to the reentrance of interlayer water. The numbered points are given in Table 1 and show the length of time the samples were retained at each condition. The results clearly show that not only had all the interlayer water

TABLE 1  
RESULTS OF TESTS ON PORTLAND CEMENT PASTES HYDRATED FOR 2½ YEARS

Condition	Relative Humidity (percent)	Water-Cement Ratio 0.6				Water-Cement Ratio 0.4			
		Time (days)	Final Weight (gram)	Percent Change From Dry	Point on Figure 1	Time (days)	Final Weight (gram)	Percent Change From Dry	Point on Figure 1
Stored	11	117	16.2645	12.33	1	56	18.6848	12.14	1
Dried incrementally beyond D-dried condition		40	14.4790	—		49	16.6627	—	
	11					4	17.2807	3.71	
	11	41	15.2587	5.39	2	45	17.4416	4.68	2
	42	20	— <sup>a</sup>	—		15	— <sup>a</sup>	—	
	11	9	15.5570	7.45	3	29	17.7717	6.66	3
	66	26	— <sup>a</sup>	—		27	— <sup>a</sup>	—	
	11	9	15.9138	9.91	4	10	18.1393	8.86	4
	84	36	— <sup>a</sup>	—		28	— <sup>a</sup>	—	
	11	28	16.2676	12.35	5	11	18.6064	11.67	5
	11	27	16.2431	12.18		—	—	—	
Immersed in saturated Ca(OH) <sub>2</sub> solution						5	20.9562 <sup>b</sup>	25.77	6
	11					22	18.5148	11.12	7
	11					9	18.5253	11.18	8
	11					17	18.5120	11.10	9

<sup>a</sup>Estimated.

<sup>b</sup>Damp dry.

reentered the sample after exposure to 85 percent RH but also it had done so progressively from low relative humidities. It should be mentioned that this result is exactly the same as that obtained by Feldman (8) when vacuum balance techniques were used and when the desiccator technique on the same sample was used. The same result has been subsequently obtained on other samples when even longer times of equilibration were used. In this case a clear differentiation of interlayer and adsorbed water was made by thermal analysis (DTA and TGA) (22).

### Density Measurements and c-Spacing

In the last section it was suggested that both water surface area and a certain density measurement are in error for the same reason; i.e., water reentering the interlayer spaces was not taken into account. This density value was used by Brunauer, Kantro, and Copeland (4) in 1958, however, with certain assumptions to calculate a c-spacing, and a value of 9.3 Å resulted. This density value (2.86 g/cc) is much higher than any listed by Taylor (23, 24) on the relationship between calcium silicates and clay minerals. In addition, Taylor lists a much lower value (2.44 g/cc) for the density of C-S-H than that published in 1956 by Brunauer, Copeland, and Bragg (6). It should be pointed out that a calculation of c-spacing from density assumes that the material is homogeneous in composition, is layered, and has a regular arrangement. As already discussed, this material does not strictly conform in at least two of these requirements—homogeneity of composition and regularity of arrangement. Thus, the calculation of the c-spacing must be considered as yielding, at best, only the average value of layer separation. As such it must still be considered as useful; revised calculations will be made.

A measured c-axis spacing of 9.3 Å is obtained by dehydrating (heating to 300 C) 11.3-Å natural tobermorite (25). Megaw and Kelsey (25) suggested that the packing of adjacent layers in the dehydrated products differed from that in 11.3-Å tobermorite; in 9.3-Å tobermorite the ribs of 1 layer were likely to pack into the grooves of the next. Brunauer, Odler, and Yudenfreund (2) assumed that the same thing occurs when C-S-H is D-dried; they state that "the layers stick to each other with such force that even soaking in water does not separate the layers. Obviously, therefore, at the relative humidity

ties of 0.07 to 0.33, used in the BET surface area determinations, water cannot enter between the layers."

It appears that the 9.3 Å value for C-S-H obtained by Brunauer, Kantro, and Copeland (4) was approximately the thickness of the layers themselves, if the layers were like tobermorite. This led to the belief that the layers had completely collapsed. Results from helium comparison pycnometry by this author (details to be published later) have shown that the measured density varies directly with water-cement ratio. The density for the D-dried C-S-H, calculated from hydrated  $C_3S$  paste prepared at a water-cement ratio of 0.5, is approximately 2.25 g/cc. The results also show that collapse on D-drying is not very great because the undried C-S-H at 11 percent RH has a density of approximately 2.34 g/cc (this value being corrected for adsorbed water). The value of the D-dried sample would be the higher if drying were accompanied by complete collapse (20, 21). The degree of collapse did not compensate for the loss in weight due to hydration; thus, this resulted in the lower density for the D-dried sample. These values correlate well with those published for various calcium silicates of the tobermorite group, where none exceeds 2.35 g/cc (23, 24).

Several comments can be made concerning the following calculations:

1. It was assumed by Brunauer, Kantro, and Copeland (4) that the density of C-S-H did not vary with preparation or Ca-Si ratio. This is contrary to assumption 1, given earlier. The observed variation in density leads to the conclusion (assuming one can calculate c-spacing from density) that c-spacing also varies with preparation and with the water-cement ratio. The measured densities would give an average c-spacing of 11.8 Å for D-dried C-S-H prepared from  $C_3S$  paste at a water-cement ratio of 0.5. This is within the range of values found by Taylor (23) for artificial tobermorites. However, the reservations stated in the preceding concerning this calculation are still maintained.

2. The collapse of a badly oriented and organized material with varying amounts of  $Ca^{++}$  ions between the layers has been assumed (4) to be similar to the collapse of natural tobermorite. It appears that the large amount of  $Ca^{++}$  ions between the layers or their poor orientation are responsible for preventing a greater collapse. It is interesting to note that nonswelling clays like vermiculite, although not the same structure as tobermorite, do allow water to reenter between the layers after they have been strongly dried (24). As has been shown by density and X-ray measurements, such materials suffer greater collapse than does C-S-H.

3. The high-density value of 2.73 g/cc obtained by Brunauer, Kantro, and Copeland (4) for the P-dried sample was high for much the same reason that the value obtained for the D-dried sample was high. A c-spacing of 10.2 Å was calculated on the basis of this density. On immersion of a P-dried sample in water during the course of a density determination, one could expect that the remainder of the interlayer water rapidly enters. Thus, the measured density will be only somewhat less than that of the layers themselves.

4. The reasoning by some authors with regard to the stoichiometry of C-S-H is considered incorrect. In 1958 Brunauer, Kantro, and Copeland (4) stated, ". . . that one molecule of  $Ca_3SiO_5$  reacts with exactly three molecules of water and one molecule of  $\beta - Ca_2SiO_4$  with two molecules of water could not be demonstrated in the present investigation. The reason for this is that a reliable method is lacking to distinguish quantitatively between adsorbed water and chemically bound water in tobermorite."

No new method has been applied by Brunauer, Odler, and Yudenfreund (2) in their recent discussion of the F-S model to separate the types of water. The original conclusion that the chemical formula of P-dried C-S-H was  $Ca_3Si_2O_7 \cdot 254H_2O$  is based

on the assumption that on reexposure to 33 percent RH neither the P-dried nor the D-dried samples experience reentry of interlayer water. This assumption has now been proved incorrect. Brunauer, Kantro, and Copeland (4) continued in their paper in 1958 that ". . . the molecular formula of the tobermorites in C-18 and D-43, corrected for adsorbed water, is  $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 2.54\text{H}_2\text{O}$ . It is clear that drying at a vapour pressure greater than  $8 \times 10^{-3}\text{mm}$  would have led to a higher water content. On the basis of arguments advanced in an earlier paper, as well as on the basis of the present results, it seems reasonable to suppose that in a saturated  $\text{Ca}(\text{OH})_2$  solution tobermorite contains 3 molecules of combined water." It is this author's opinion that the formula  $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$  should be considered as not having been established; a sounder based estimation can, however, be made.

It will first be shown that the area of the internal plus external surfaces of D-dried C-S-H, usually taken as  $755 \text{ m}^2/\text{g}$ , is of the right order. This is the value generally assumed for one layer of C-S-H.

In a recent paper, Feldman (8) showed that the total interlayer water for a sample of hydrated portland cement was 7.54 percent by weight of D-dried material, with the sample having a nitrogen area of  $30 \text{ m}^2/\text{g}$ . If it is assumed that the interlayer water molecule covers  $10.8 \text{ \AA}^2/\text{molecule}$  on 1 surface, the internal area is  $274 \times 2 \text{ m}^2/\text{g}$  (i.e.,  $548 \text{ m}^2/\text{g}$ ) and, if nitrogen measures the external area correctly, the total area is thus  $578 \text{ m}^2/\text{g}$ . If corrections are made for incomplete hydration, the equivalent total area is thus  $670 \text{ m}^2/\text{g}$ . If one assumes that completely hydrated Type II portland cement is composed of 80 percent C-S-H (27) and assigns the area of internal plus external surface of  $755 \text{ m}^2/\text{g}$  to the C-S-H portion, the expected value of surface area would be 80 percent of  $755 \text{ m}^2/\text{g}$  (i.e.,  $604 \text{ m}^2/\text{g}$ ). This agrees fairly well with the  $670 \text{ m}^2/\text{g}$  figure when one considers that in hydrated portland cement some of the water generally termed "interlayer" may have come from the aluminates and sulfoaluminates.

A further series of calculations may be used to establish the stoichiometry and the calculated c-axis spacing of C-S-H derived from  $\text{C}_3\text{S}$ . Hydrated  $\text{C}_3\text{S}$  pastes, when first D-dried from about 12 percent RH by Helmuth (19), yielded a water content of approximately 28.4 percent of the ignited weight. According to Brunauer, Kantro, and Copeland (4) and to Feldman (8), at 12 percent RH the sample contains approximately all the interlayer and 1 monolayer of adsorbed water. Hydrated  $\text{C}_3\text{S}$  paste, containing C-S-H dehydrated to  $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  (approximately D-dried), contains 19.7 percent water based on the ignited weight. The difference between 28.4 and 19.7 percent (8.7 percent) is made up of the interlayer and the adsorbed water. For a surface area of  $73 \text{ m}^2/\text{g}$  determined by this author on 0.5 water-cement ratio paste with nitrogen adsorption, the equivalent value of a monolayer of water is 2.0 percent by weight, leaving 6.7 percent as interlayer water. This corresponds to 1.7 molecules per formula unit at about 12 percent RH. This gives a formula of  $\text{Ca}_{3+x}\text{Si}_2\text{O}_7 \cdot 3.7\text{H}_2\text{O}$  for this C-S-H at 12 percent RH. For a molecule coverage of  $10.8 \text{ \AA}^2/\text{molecule}$ , the 6.7 percent interlayer water is equivalent to  $244 \times 2 = 488 \text{ m}^2/\text{g}$  of internal area. Adding internal to external area previously calculated made a total area of  $561 \text{ m}^2/\text{g}$ . One gram of hydrated  $\text{Ca}_3\text{SiO}_5$  paste on the ignited weight basis contains 0.71 g of D-dried C-S-H, giving the expected value of  $755 \times 535 \text{ m}^2$ . This compares well with the  $561 \text{ m}^2$  in the preceding. When only 1 molecule of interlayer water per formula unit is used for the calculation instead of 1.7 molecules, a value of only  $357 \text{ m}^2/\text{g}$  is obtained as the total surface area. (In the formula, x represents the variation that is normally found from Ca-Si ratio of 3 to 2.)

Assuming the composition at 12 percent RH to be  $\text{Ca}_{3+x}\text{Si}_2\text{O}_7 \cdot 3.7\text{H}_2\text{O}$ , assuming, as Brunauer, Kantro, and Copeland (4) did, that a unit cell contains a formula unit and that it is orthorhombic with  $\underline{a} = 5.59 \text{ \AA}$  and  $\underline{b} = 3.64 \text{ \AA}$ , and using a value of  $2.34 \text{ g/cc}$

for density, one obtains the value of the average c-spacing of 12.4 Å, as opposed to 11.8 Å for the D-dried C-S-H prepared from C<sub>3</sub>S paste at a water-cement ratio of 0.5. This value of 12.4 Å must be regarded as tentative for some assumptions that were in the calculation. The preceding calculation of average c-spacing is still subject to the previously mentioned reservations with regard to homogeneity in spacing and composition.

Another interesting point about hydrated C<sub>3</sub>S paste was observed by Helmuth (19). After the paste was D-dried and reexposed to water vapor, the total water content at 12 percent RH was approximately 25.5 percent or 2.9 percent less (on the ignited weight basis) than that found from the desorption branch. When the paste was exposed to increasing humidities as high as approximately 100 percent RH and then returned to 12 percent RH, all the water initially present was regained. This evidence, which is similar to that for portland cement as shown in Figure 1, shows clearly that the interlayer water had completely reentered the sample.

### Phenomena Related to Hydraulic Radius of Hydrated Portland Cement

Brunauer, Odler, and Yudenfreund (2) presented the calculations, based on the concept of hydraulic radius, as evidence against the F-S model. Table 1 in the paper by Brunauer, Odler, and Yudenfreund gives the hydraulic radius of the pores not penetrable by nitrogen as being much larger than the diameter of the nitrogen molecule. Faced with the question of why nitrogen cannot enter these pores, Mikhail, Copeland, and Brunauer (28) suggested that these pores have necks smaller than the diameter of the nitrogen molecule. This conclusion was based on the assumption that the interlayer water did not reenter the D-dried sample. Brunauer, Odler and Yudenfreund concluded that the values they derived in column 10 of Table 1 in their paper (2) for the "internal" hydraulic radius are too large to be attributed to water occupying interlayer spaces. This author suggests that in references to interlayer spaces, however, other calculations would have been more appropriate. Because the area of a sheet of C-S-H, according to Brunauer, Kantro, and Copeland (4), is 755 m<sup>2</sup>/g, the interlayer area would be 755 S<sub>N<sub>2</sub></sub> and not S<sub>H<sub>2</sub>O</sub> - S<sub>N<sub>2</sub></sub> as used by Brunauer, Odler, and Yudenfreund (2). If the figure is corrected for Ca(OH)<sub>2</sub> in the hydrated portland cement, the interlayer area per gram would be approximately 600 - S<sub>N<sub>2</sub></sub> and the hydraulic radius should be calculated by the expression  $V_{H_2O} - V_{N_2}/600 - S_{N_2}$ .

In this calculation the correction for Ca(OH)<sub>2</sub> giving the amount of C-S-H gel in hydrated portland cement was due to Powers (27); this was approximately 80 percent of the hydrated cement. No correction was made to 755 m<sup>2</sup>/g for the other components because they are considered to be incorporated with the C-S-H gel. However, it is clear that corrections for other components would be minor and would not alter the results significantly. Table 2 gives calculations made according to this mode for hydraulic radius of the pastes cited by Brunauer, Odler, and Yudenfreund (2).

TABLE 2  
SURFACES, POROSITIES, AND HYDRAULIC RADII OF PORTLAND CEMENT PASTES

Water-Cement Ratio (1)	S <sub>N<sub>2</sub></sub> (m <sup>2</sup> /g) (2)	600 - S <sub>N<sub>2</sub></sub> (3)	V <sub>H<sub>2</sub>O</sub> (ml/g) (4)	V <sub>N<sub>2</sub></sub> (ml/g) (5)	V <sub>H<sub>2</sub>O</sub> - V <sub>N<sub>2</sub></sub> (ml/g) (6)	r <sub>1a</sub> Brunauer (Å) (7)	r <sub>1a</sub> Corrected (Å) (8)
0.35	56.7	543.3	0.1264	0.0748	0.0516	3.4	0.95
0.40	79.4	520.6	0.1776	0.1059	0.0717	5.8	1.38
0.50	97.3	502.7	0.2615	0.1792	0.0823	8.5	1.64
0.57	132.2	467.8	0.3110	0.2493	0.0617	10.0	1.32
0.70	139.5	460.5	0.4008	0.2758	0.1250	20.8	2.78
Montmorillonite	15	735 <sup>a</sup>	—	—	0.0964	—	1.26

<sup>a</sup>750 - 15 = 735.

Column 7 gives the calculations from Table 1 in Bruno, Odler, and Yudenfreund's paper (2) and column 8 gives the suggested corrected values. Also included is a calculation for montmorillonite, a well-known layer-structured clay. The similarity between the average of the first 4 pastes, 1.32 Å, and montmorillonite, 1.26 Å, is very significant. The 0.7 water-cement ratio paste gives a value of 2.78 Å (col. 8) which is much lower than that given in column 7. This author believes, however, that the value in Table 1 (2)  $V_{H_2O} - V_{N_2}$  for this paste is much too high. The values of  $S_{H_2O}$  and  $S_{N_2}$  for water-cement ratios of 0.57 and 0.70 in the same table are almost the same, and there is no trend of  $V_{H_2O} - V_{N_2}$  increasing with water-cement ratio. Furthermore, this author has made determinations on 14 different preparations at a water-cement ratio of 0.8 and has found that for these the value for  $V_{H_2O} - V_{N_2}$  varied between 0.06 and 0.08. Thus, it is thought that the hydraulic radius of the water-cement ratio 0.7 paste would also be similar to that of montmorillonite. The hydraulic radius, then, gives further supporting evidence of the interlayer nature of the so-called gel water.

### LENGTH- AND WEIGHT-CHANGE ISOTHERMS

#### The Question of D-Drying

The writer has now cited considerable evidence to indicate that the D-dried samples do allow water to reenter between the layers. It has been argued (2), however, that the samples discussed in Feldman's recent work (8) were not properly D-dried and that this fact explains his results. The following points should clearly establish that the samples were D-dried.

1. The amount of water removable from a state in equilibrium with a relative humidity of 11 percent was determined by conventional D-drying. It was then found that heating replicate samples at 85 C for 3 hours in a thermal balance under high-vacuum conditions gave an equivalent weight loss. One sample was heated at 95 C for 3 hours and at 97 C for 2 hours more without any major change in the weight loss.

2. The vapor pressure at the "dry" condition was measured with a sensitive Bourdon gage of 1 $\mu$  repeatability. It indicated a pressure of less than 1 $\mu$ .

3. Helmuth (19) on measuring isotherms of hydrated  $C_3S$  paste dried the samples (in the form of 1-mm thick specimens) for 3 months by conventional means. His results for both sorption and length-change isotherms were qualitatively and quantitatively similar to those of Feldman (8); they showed similar hysteresis, complete regain of interlayer water, and irreversibilities of length and weight change.

4. Brunauer, Odler, and Yudenfreund (2) also argued that the nitrogen areas published by the present writer (8) suggested that his samples were not D-dried. In point of fact, the paste sample hydrated at a water-cement ratio of 0.5 was D-dried by the conventional method for determining surface area by nitrogen adsorption. Then the sample was heated to progressively higher temperatures (up to 400 C) and the area measured at each temperature decreased from 47 to 42 m<sup>2</sup>/g. Tomes, Hunt, and Blaine (29), working with pastes that were 50 percent hydrated at a water-cement ratio of 0.5, obtained surface areas by nitrogen adsorption of 10 to 25 m<sup>2</sup>/g, a maximum surface area of 50 m<sup>2</sup>/g for complete hydration; a value of 97 m<sup>2</sup>/g was obtained by Mikhail, Copeland, and Brunauer (28) and republished by Brunauer, Odler, and Yudenfreund (2).

It is not being suggested here that the value of 97 m<sup>2</sup>/g is incorrect but rather that nitrogen area can be affected by several factors. These may include water-cement ratio, admixture dosage, and perhaps alkali and sulfate content. This suggests the importance of nitrogen area and of its proper interpretation. With this valuable tool one can detect the sensitivity of hydrated portland cement to various agents and

understand its variability in relation to the mechanical and physical properties of the hydrated cement. Certain trends in properties of hydrated portland cement are functions of water-cement ratio and admixture addition. It is interesting to observe that as water-cement ratio increases the nitrogen area increases, the Ca-Si ratio decreases, and the first drying shrinkage and density increase. Large dosages of some admixtures (e.g., calcium lignosulfonates) enhance the effect of high water-cement ratio. The nitrogen area reflects the change in Ca-Si ratio and predicts differences in first drying-shrinkage properties.

### Scanning Loops

Data used in developing the F-S model (1) indicate that interlayer water reenters D-dried samples in increments as the relative humidity they are exposed to increases. When some water reenters the interlayer spaces at, for example, 30 percent RH, it goes on sites that will retain it to a very low RH. Thus, one obtains an irreversibility in the isotherm, a scanning loop (8). This is probably caused by the collapsed layers mechanically blocking the water from entry to high-energy sites; the layers, however, subsequently reopen. One may refer to this as a changing nature of the adsorbent. One of the assumptions made in adsorption equations is that the adsorbent surface remains constant qualitatively and quantitatively. In contrast, the water-scanning isotherms of weight and length change showed that the interlayer water reenters at very low humidities and right through the BET range. Naturally then, any calculation of the monolayer capacity using this isotherm will be incorrect. A similar difficulty occurs in an attempt to calculate the surface area of some montmorillonites from water vapor adsorption.

In addition, above 7 percent RH a quantitative separation of the interlayer and physically adsorbed water was made through interpretation of the scanning isotherms. It was also made clear that, even below 7 percent RH, a considerable portion of the water put on by the sample was interlayer. The use of a trial-and-error procedure or, alternatively, the assumption that the nitrogen area was approximately correct has shown that (a) the Gibbs and Bingham equations (30) properly described the length change and sorption data for physical adsorption; and (b) calculation of Young's modulus of the solid material from the length-change adsorption data yielded a value of  $4.35 \times 10^6$  lb/in.<sup>2</sup>, which is very similar to that obtained by direct measurement of E as a function of porosity and extrapolation to zero porosity,  $4.5 \times 10^6$  lb/in.<sup>2</sup> The latter work was done by Helmuth and Turk (31) and they concluded that the interlayer spaces are "gel pores." In their extrapolation they considered the porosity to be that obtained by water saturation methods, not recognizing that the water reentered between the layers causing a higher porosity. Soroka and Sereda (32) confirmed the work of Helmuth and Turk and made a similar extrapolation. Verbeck and Helmuth (15) reassessed this work. They then came to the conclusion that gel pores were interlayer spaces, and so their new extrapolation excluded these spaces. Brunauer, Odler, and Yudenfreund (2) refer to the work of Soroka and Sereda (32), state that "Feldman rejects the values of his colleagues," and find an inconsistency in this. Subsequent to the submission of the Soroka and Sereda paper (32), this author (8) found that the total volume of interlayer water derived by calculation from scanning isotherms was approximately equal to the difference between the total volume of water sorbed and the total volume of nitrogen or methanol, as given by the following:

$$V_{(H_2O)} - V_{(N_2 \text{ or methanol})} = V \text{ (interlayer water)}$$

Subsequently, this author obtained helium comparison pycnometry data (21) indicating that helium occupied essentially the same volume as methanol.

When the physically adsorbed water is deducted from the observed adsorption isotherm, one obtains an isotherm showing how the interlayer water reenters as a function of RH. This enabled Feldman and Sereda to propose the model that emphasizes the inter-relationship of  $E$ ,  $\Delta w/w$ ,  $\Delta \ell/\ell$ , and RH (1).

### Reversibility and Equilibration Time

The question of reversibility is always related to that of equilibration time. If weeks were allowed for equilibration, months or years could be suggested if one did not wish to accept the data. In the following paragraphs, data cited by this author (8) are used to counteract this type of argument. In these paragraphs also is a substantiation of the conclusion that there are 2 processes occurring simultaneously. One is essentially in thermodynamic equilibrium with the water-vapor pressure and involves adsorption on the same surfaces on which nitrogen adsorbs. This occurs fairly rapidly and is represented by the scanning loops. The other process involves intercalation of the layers and strong attachment to internal surfaces. The latter process is slow and does not represent a path of thermodynamic equilibrium and is not reversible. At lower humidities (below 50 percent RH), the process, to all practical purposes, ceases at the various RH steps. The system is not in "thermodynamic" equilibrium with the relative vapor pressure at those points.

1. The experimental points were very closely spaced. When the pressure was changed by a small increment, a very rapid increase of weight took place and was followed by a very slow rate. Equilibrium was judged not only by weight change but by pressure change, pressure being measured with a sensitive Bourdon gage with repeatability of  $1 \mu$ . A pressure change of less than  $10 \mu$  a day was used as the pressure criterion for equilibrium. Below 50 percent RH on the adsorption loop, 2 to 3 days per closely spaced point were adequate to meet this criterion

2. Figure 1 in Feldman's paper (8) shows isotherms and numbered scanning loops. Loops 2, 5, 6, 7, and 8 show clearly how, after desorption on the loop, the readsorption meets the exact point on the main curve where the loop commenced; in the case of loop 7 the complete cycle took  $3\frac{1}{2}$  weeks.

3. On the main desorption curve, loops 9 and 10 also return exactly through the point they started from 1 week earlier. If they were so far removed from an equilibrium position, it seems unlikely that they would have rejoined; instead the point would have been well below at the same pressure on the return of the loop.

4. It was found that, in a preliminary experiment on the desorption curve using 7 days per point, there was no change after 1 day of using high-vacuum conditions. The data shown in Figure 1 and given in Table 1 of this paper support this indication; from 100 percent RH to 11 percent RH, no further change was observed beyond the first measurement taken after 2 weeks. Further conditioning of  $1\frac{1}{2}$  months at this point produced no further change.

5. It is clear from the length-change data that the 2 types of water separated by scanning loops are completely different and that the  $(\Delta \ell/\ell)/(\Delta w/w)$  relationship for the interlayer water is 4 times that for the physically adsorbed water. The length change due to physically adsorbed water is governed by the Gibbs and Bangham equations. When the interlayer water reenters, a considerably larger expansion per unit weight of adsorbed water than that predicted by these equations must be expected. Work in the same paper by Feldman (8), using methanol as adsorbate, shows that there is also interlayer penetration by methanol, although not nearly to the same extent as by water. Contrary to what is generally felt about methanol and length change caused by its sorption on hydrated portland cement, however, the  $(\Delta \ell/\ell)/(\Delta w/w)$  is larger for the inter-

layer penetration of methanol than of water. This, of course, is not surprising on the basis of molecular sizes.

6. The isotherms of both length and weight change for water sorption on hydrated portland cement have been measured with great precision and detail (8) in a high-vacuum apparatus using exceedingly sensitive measuring devices. Water isotherms have been previously published by many authors (33, 34, 35) including Powers and Brownyard (36), and recently Helmuth (19), Mikhail, Kamel, and Abo-el-enein (37) with none of them exhibiting closing secondary hysteresis loops (neither does the isotherm shown in Figure 1 of this paper).

The early work of Powers and Brownyard (36) is almost completely devoid of desorption isotherms although this is not generally realized. There are, however, 2 such curves and the following statements are made:

As shown in Figure 2-6, the adsorption and desorption curves coincided only at pressures below 0.10 p<sub>s</sub>. (As a matter of fact, it is not certain that the curves coincided over this range, but it seems probable that they did so. Powers and Brownyard then show (in essence) some scanning isotherms and continue.) Although the phenomenon has not been investigated extensively here, there is little reason to doubt that portland cement pastes all show essentially the behaviour described above. This matter of hysteresis is significant. . . . At any rate the whole phenomenon cannot be understood until these loops can be adequately interpreted. However, practically all the measurements reported in this paper were of adsorption only. Therefore, the interpretation of the adsorption curve is the only part of the problem that can be considered here.

It is now clear that without complete understanding of these loops the adsorption curve could not be interpreted either.

In addition, in the work by Powers and Brownyard, the point at approximately 10 percent RH on first drying was reattained after further drying and a subsequent cycle of wetting and redrying to the above humidity. This means that all the water, including the interlayer water that had been removed, reentered during rewetting.

Helmuth (19) D-dried from low humidities continually for 3 months and, in his work as stated previously, all the interlayer water also returned. This, it must be reemphasized, is a crucial point as has been pointed out by others (2).

Helmuth's results (19) on C<sub>3</sub>S paste contain a further interesting point. The desorption isotherm appeared to rejoin in the primary hysteresis region at high humidities, but as desorption continued there reappeared a very large secondary hysteresis equal in magnitude to that of this author's at the lower humidities. The preceding behavior is probably related to the primary hysteresis and may involve recrystallization of Ca(OH)<sub>2</sub> and a changing of the pore size, shape, and distribution. This might explain the unpublished work of J. Hagymassy referred to by Brunauer, Odler, and Yudenfreund (2).

Mikhail, Kamel, and Abo-el-enein (37) have recently published water isotherms on various cement hydration products. In every case large hysteresis loops were obtained without any closure. Mikhail, Kamel, and Abo-el-enein found that only 48 hours were necessary between successive measurements. On samples prepared in paste form, Mikhail states that 12 days should be allowed between measurements. The experimental points, however, are spaced quite far apart, e.g., from 15 to 35 percent RH. He also states, "Desorption was then carried down to extremely low relative pressures. The sample was then exposed to out-gassing at 30° C for a period of 30 hours, to remove all the adsorbate and the sample weight was brought back to its original value."

7. Numerous data have been compiled by this author since the International Symposium work (8). The data were obtained after allowing much longer times for equilibrium (in the order of months) in both high-vacuum apparatus and in desiccators and by using the same samples. Some of the data are shown in Figure 1 and given in Table 1. They have confirmed the existence of scanning loops, the equilibrium of sorption points, and the complete reentry of interlayer water after very severe drying and after a cycle of rewetting and drying to 11 percent RH.

8. The accepted method for D-drying has been worked out and published by Copeland and Hayes (38) who state that it takes 4 to 7 days for equilibrium. This involves drying from fairly wet conditions to removal of both the tightly held first layer and the even more tightly held interlayer water from the very narrow spaces. The slower-than-normal times required for equilibrium of water during the adsorption stage is probably due to the lengthy process of reopening the layers.

#### NEW EXPERIMENTAL EVIDENCE

Recently this author has done an entirely new type of work (20, 21, 22) that not only provides further evidence for the F-S model but also provides powerful new techniques to study hydrated cement. A few of the results will be briefly discussed.

1. When water is removed from C-S-H materials, the prime concern is what happens to the spaces vacated by the water and what happens to the solid. A method of studying the spacing is to measure rates of diffusion of helium gas (a small atom) into them (20). When hydrated portland cement equilibrated for several months at 11 percent RH was exposed to helium, helium very quickly entered the pores of even 20 Å radius. When the gas was compressed to 2 atmospheres, rate curves could be measured for helium diffusing into the vacated spaces. As water was removed incrementally from the sample, the diffusion rate and absolute quantity at each water content increased at first; but as more water was removed, the rate decreased although the quantity continued to increase. Finally, the quantity also decreased, and at D-dry conditions the diffusion rate was very low. These results can best be explained by the collapse of layers in the same manner as the F-S model has suggested (1). On readsorption of water, the helium diffusion rate again increased. After the sample was exposed to high humidities, all the interlayer water had reentered (diffusion experiments were performed at 11 percent RH), and the rate curves were similar to the curves obtained for the sample at the beginning of the experiment. These results indicate that the layers had reopened and that interlayer water had reentered; if it had not, the very low diffusion rate observed at the D-dry condition would have remained the same.

2. Density measurements (21) obtained by a helium penetration technique from hydrated portland cement prepared at water-cement ratios of 0.4 to 1.0 showed that the computed densities of C-S-H gel vary with water-cement ratio from approximately 2.30 to 2.18 g/cm<sup>3</sup>. For water-cement ratios of less than 0.6, the density decreased with decreasing water-cement ratio. Because Ca-Si ratio and nitrogen surface area vary with water-cement ratio, one might reasonably expect changes in density and degree of collapse.

3. Measurement of solid volume and length simultaneously as a function of water content on drying to the D-dried position and on rewetting has enabled an independent calculation of the monolayer capacity for water to be made. On the assumption that

$$\Delta V/V - 3\Delta l/l = \Delta w/V$$

where

- $\Delta V/V$  = relative change in volume of solid phase plus adsorbed phase,  
 $\Delta l/l$  = external length change,  
 $\Delta w$  = change in volume of adsorbed water, and  
 $V$  = volume of solid,

it was found that the results for D-dried samples yield a surface area varying only by about 15 percent from the result obtained by nitrogen adsorption. Results also suggested that first D-drying reduces the surface area of the hydrated portland cement.

This last group of experiments (20, 21) presents evidence different, and perhaps in a superior form, from that obtained from conventional isotherms. The latter experiments indicate how much water entered or left the specimen; but in these new experiments, as in length change studies, information is gained also about the effect of the removal of the water on the solid body. Thus, it is possible to draw conclusions as to where the water was likely to have come from, the nature of the spaces it occupied, and its role in the structure of the solid.

4. Thermal analysis both DTA and TGA (22) were performed on samples equilibrated at a relative humidity for lengths of time, in the order of months in desiccators, and at relative humidities similar to those reported here for the isotherms. It was found that interlayer water and its reentry could be correlated to an endothermic effect at 90 to 105 C, and the physically adsorbed water to an effect at 65 to 80 C. The results confirmed the fact that 11 percent RH was a nonunique state and also confirmed the conclusions in the previous section concerning scanning loops, equilibration, and hysteresis.

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