

The New Model of Hardened Portland Cement Paste

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Feldman and Sereda reject the Powers model of the structure of hardened portland cement paste on the ground that the BET surface area and the porosity of D-dried pastes as measured by water vapor adsorption is wrong because four-fifths of the uptake of water is interlayer water and not adsorbed water. They propose that nitrogen adsorption measures the surface approximately correctly and, on the basis of these ideas, present a new model of paste structure. The present paper shows that water vapor adsorption measures the surfaces and porosities of D-dried pastes correctly, whereas nitrogen measures only part of the surface and porosity. D-dried pastes have no interlayer water nor adsorbed water. Pore structure analysis shows that nitrogen cannot penetrate into many large pores. Completely hydrated D-dried pastes of the same cement have the same surface area when measured by water adsorption regardless of w_0/c , whereas nitrogen areas vary by a factor of almost 3. The data of Feldman and Sereda show that their quick-drying procedure is approximately equivalent to P-drying. P-dried pastes contain both interlayer water and adsorbed water. The energies of binding of these 2 types of water strongly overlap; consequently, they cannot be separated by tests of reversibility. Furthermore, because of the different drying procedure, no conclusion can be drawn from the experiments of Feldman and Sereda for D-dried pastes. The authors of the new model contend that no equilibrium is reached in the surface area measurements by water adsorption on D-dried pastes. It is shown in the present paper that equilibrium was reached in these measurements but was not reached in most of the experiments of Feldman and Sereda. Their desorption isotherms, as well as the loops, by which they attempt to test reversibility, represent nonequilibrium conditions. The main conclusion of the paper is that the authors know of no properly interpreted evidence to date that contradicts the Powers model.

•RECENTLY A NEW MODEL of the structure of hardened portland cement paste has been presented by Feldman and Sereda (1) to replace the old model, called the Powers model. Although much has been added to the original ideas of Powers by his co-workers at the Portland Cement Association, by himself, and by other researchers all over the world, the basic ideas of the model have remained unchanged. The model proposed by Powers and Brownyard (2) achieved an immediate success by correlating 2 physical properties, the surface area and the porosity of the paste, with vital engineering properties such as strength, volume changes, and permeability. The correlation was semi-empirical; further research has removed much of the empiricism and has brought about a more fundamental understanding of the structure of paste.

The surface area and the porosity of the paste were measured by the BET method (3) using water vapor as the adsorbate not only by Powers but by many others, including Brunauer and his co-workers. Feldman and Sereda attempt to show that the use of water vapor for measuring the surface areas and porosities of cement pastes is wrong, and that the correct or almost correct values are obtained by nitrogen adsorption. If this statement is correct, the Powers model falls or must be greatly modified. If the statement is wrong, the model of Feldman and Sereda falls or must be greatly modified.

WATER SURFACE VERSUS NITROGEN SURFACE

The problem of water versus nitrogen surface area was settled by Brunauer, Kanthro, and Weise 10 years ago in a paper on the surface energy of tobermorite gel (4). The name tobermorite gel is being replaced now by the less definite term C-S-H gel. The gel is the calcium silicate hydrate produced in the paste and "bottle" hydration of tricalcium silicate (Ca_3SiO_5 or C_3S) and β -dicalcium silicate ($\beta\text{-Ca}_2\text{SiO}_4$ or C_2S); it is also produced in the ball-mill hydration of C_2S . On the basis of Bernal's suggestion, Brunauer named these hydrates of varying composition simply tobermorites; later, on the suggestion of H. F. W. Taylor, he changed the name to tobermorite gel and abbreviated it in some of his papers to tobermorite (G). Because in the present paper numerous references will be made to the papers of Brunauer and his co-workers, the name tobermorite gel will be retained to avoid confusion.

One of the most basic facts of surface science is that atoms, ions, or molecules in the surface have higher energies than those in the body. These excess energies were first calculated by Born and Stern (5) 10 years before the first experimental determinations were made, and all of the numerous theoretical calculations and all of the numerous experimental determinations that have been made since 1919 have led to the same result. The experimental demonstration is very simple: If a substance appears in 2 different states of subdivision, the one with the higher specific surface area has the higher heat of solution.

Brunauer, Kanthro, and Weise (4) made 14 different preparations of tobermorite gel by hydrating C_3S and C_2S in different ways, and plotted the heats of solution against the specific surface areas. The slope of such a plot gives the surface energy, which is usually expressed in erg/cm^2 . The surface areas were measured by water vapor adsorption for samples of all 14 preparations and by nitrogen adsorption for samples of 8 preparations. The water areas ranged from 244 to 376 m^2/g . In an earlier work, one of the present authors calculated the specific surface area from crystal structure data (6). He showed that if the tobermorite gel sheets are 2 molecular layers thick, the surface area should be 377 m^2/g ; if they are 3 molecular layers thick, it should be 251 m^2/g . The values experimentally obtained were closer to these limits than the experimental error. Here is then a strong indication that water adsorption measures the true surface of tobermorite gel. The external plus interlayer surface of tobermorite gel is 755 m^2/g .

The nitrogen surface areas ranged from 100 to 21 percent of the areas measured by water. Whereas the water areas correlated excellently with the heats of solution, the samples with higher surface giving higher heats of solution, there was no such correlation with the nitrogen surface areas. The authors concluded: "That nitrogen does not measure the true surface of tobermorite can be seen from the following considerations. As Figure 1 shows, the heat of solution of tobermorite in D-35 is about 8 cal/g larger than that of the tobermorite in D-28, but the surface area of the former is only about half as large, as measured by nitrogen adsorption (Table VI). This would indicate a negative surface energy, an absurdity. Several other pairs of preparations would, likewise, lead to negative surface energy values." It may be added that nitrogen adsorption for some of these pairs indicated not merely negative surface energies, an absurdity in itself, but large negative surface energies.

The explanation of the nitrogen results is simple. The heats of solution measure the excess energy residing in the entire surface, whereas nitrogen adsorption measures only a part of the surface, which leads to the absurd negative surface energies. In contrast, the water surface areas gave a positive surface energy of 386 erg/cm^2 . This an interesting figure.

Earlier, Brunauer, Kantro, and Weise determined the surface energy of calcium hydroxide (7) and hydrous amorphous silica or silanol (8). The value of the former is 1,180 and of the latter, 129 erg/cm². The surface areas were measured by nitrogen adsorption, which is an important point to be noted.

The surface energy of a substance depends on the nature and the geometric arrangement of the surface. The calcium hydroxide consisted of almost perfect crystals; the hydrous silica was completely amorphous. Tobermorite gel is intermediate between these extremes; it is very poorly crystallized, and its X-ray diffraction pattern consists of only 3 lines. In addition, the calcium silicate hydrate is what Brunauer has called with some license a "chemical mixture" of calcium hydroxide and hydrous silica. On the basis of these 2 facts and also on theoretical grounds, one can predict that the surface energy of tobermorite gel should be roughly the geometric mean of the surface energies of calcium hydroxide and hydrous amorphous silica. The figure obtained for tobermorite gel on the basis of water surface areas was very close to that.

In later work, the same authors redetermined the surface energy of tobermorite gel (9). The original work was based on 14 preparations—7 obtained by the hydration of tricalcium silicate and 7 obtained by the hydration of dicalcium silicate. The later work was based on 70 C₂S pastes, 58 C₃S pastes, and 27 alite pastes. Not only was the sample larger, but also the theoretical evaluation was more accurate. The new value was 450 erg/cm²; still roughly the geometric mean of the surface energies of calcium hydroxide and hydrous amorphous silica. Furthermore, the lowest surface measured for any of about 150 mature pastes was 243 m²/g, and the highest was 387 m²/g; values still within experimental error were those calculated by Brunauer from X-ray data for tobermorite gel sheets consisting of 3 and 2 molecular layers respectively. These data are in line with electron microscopic observations, which indicate that the thickness of the sheets is the order of a unit cell. (In the new model, the thickness of the sheets is around 15 molecular layers.) In the early stages of hydration, higher surface areas were obtained, ranging up to nearly 600 m²/g, indicating that the gel also contained sheets of a single molecular layer.

The conclusion from all this is that nitrogen adsorption measures only a part of the surface, whereas water vapor measures the true and correct surface. A corollary of this conclusion is that at p_0 , the saturation pressure of the vapor, water measures the total porosity of the paste, whereas nitrogen measures only a part of the porosity.

It may be worth mentioning that Wittman determined the surface energy of completely hydrated cement paste by a much less accurate method than that described above, and obtained a very rough value of 400 erg/cm² (10). The main interest in this work is that both the theoretical approach and the experimental approach were totally different from ours. If the surface of tobermorite gel were less than one-fifth as large as that measured by us, which is the contention of the new model, the surface energy would be more than 5 times as large as ours, roughly 2,300 erg/cm², or twice as large as that of Ca(OH)₂. There is no surface energy in the literature as high as this value.

This brings up the question as to whether the tobermorite gel in portland cement pastes has the same surface area as in pastes of the calcium silicates. The question was answered long ago, but the results were not published. Verbeck obtained excellent water adsorption data for numerous completely or almost completely hydrated portland cement pastes of widely differing compositions at a relative humidity of 36 percent. For many of these pastes v_m values were also available; these values represent the number of molecules necessary to cover the entire surface with a single adsorbed layer. It was found that the adsorption at 36 percent relative humidity and v_m differed by a very nearly constant factor—a result that a surface chemist would expect. By least squaring Verbeck's data and using the constant factor, Brunauer calculated the average specific surface area of the tobermorite gel produced by C₃S and C₂S in the hydration of portland cements. Not only were the results within the range of 2- and 3-layer tobermorite sheets discussed earlier, but also the calculated area produced in the hydration of C₂S was significantly lower than that produced by C₃S. This was in complete agreement with the results obtained in the hydration of C₃S and C₂S; and later Kantro, Brunauer, and Weise advanced a mechanism of the hydration process that explains the fact that tobermorite gel in C₃S pastes has a higher specific surface area than in C₂S pastes (11).

All surface areas discussed were obtained for D-dried pastes. This designation is applied to pastes equilibrated at the vapor pressure of ice at -78°C , which is 5 by 10^{-4} mm of mercury. Another type of drying, designated as P-drying, will also be discussed. This applies to pastes dried at the equilibrium vapor pressure of magnesium perchlorate dihydrate and tetrahydrate, which is 8 by 10^{-3} mm of mercury. Because the vapor pressure at P-drying is 16 times as high as that at D-drying, the drying is less complete; and it will be seen that at D-drying all adsorbed water is removed, whereas at P-drying a considerable amount of adsorbed water remains on the surface.

The question may be legitimately raised as to whether D-drying alters the surface area of the cement paste. This question is not pertinent to the present discussion, because Feldman and Sereda also performed their experiments on samples that were subjected to what they called the "equivalent" of D-drying (more about this later). Nevertheless, the question is of considerable interest.

In the first drying of a cement paste, the total porosity decreases, and the evaporable (or adsorbed) water decreases. It is possible, therefore, that the surface area also decreases; in other words, the surface areas measured by water adsorption on D-dried samples may possibly be lower than the surface areas of undried pastes. There is, however, an important indication that this is not so. Powers and his co-workers determined the surface areas of 4 undried, saturated pastes by permeability measurements, each at 4 different temperatures, and obtained remarkably close agreement with the BET areas obtained by water vapor adsorption after D-drying of the pastes. For the 4 pastes, prepared with water-cement ratios of 0.4, 0.5, 0.7, and 0.8, the permeability areas were 525, 525, 525, and $500\text{ m}^2/\text{cm}^3$ respectively, and the BET areas were 528, 524, 517, and $524\text{ m}^2/\text{cm}^3$ respectively. The porosities of the 4 pastes were 0.391, 0.467, 0.510, and 0.554 respectively. These results have not been published as yet.

One other important experiment will be mentioned before we pass to a different subject. Copeland determined the specific surface area of a paste by small angle X-ray scattering, and obtained almost exact agreement with the surface area of the D-dried paste (measured, of course, by water vapor adsorption).

THE PROBLEM OF INTERLAYER WATER

Feldman and Sereda contend that about four-fifths of the adsorbed water in D-dried samples is interlayer water, i. e., water between the molecular layers inside the tobermorite gel sheets. Feldman (12), aware of our results that show that D-dried samples do not soak up water even when immersed in water (6), explained this by stating that the interlayer water was already inside the gel sheets before we immersed the sample in water. However, he failed to consider the other results in the same paper. The density of the tobermorite gel showed that the spacing between the layers, the c-spacing, was 9.3 \AA , which is the distance of closest approach between the calcium silicate hydrate layers. At this distance, there is no interlayer water in the sheets. Furthermore, the layers stick to each other with such force that even soaking in water does not separate the layers. Obviously, therefore, at the relative humidities of 0.07 to 0.33, used in the BET surface area determinations, water cannot enter between the layers.

The chemical formula of D-dried tobermorite gel, which has a molar CaO/SiO_2 ratio of 1.5, is $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. Bernal proposed the structural formula of $\text{Ca}_2[\text{SiO}_2(\text{OH})_2]_2[\text{Ca}(\text{OH})_2]$, which is only partly correct (13). On the basis of our experience of about a decade and a half, a more correct representation would be $\text{Ca}_2[\text{SiO}_2(\text{OH})_2]_2[x(\text{CaO} \cdot \text{H}_2\text{O})]$, where x may be more or less than 1. When the CaO/SiO_2 ratio is 1.5, x is equal to 1, but it would be erroneous to write $\text{Ca}(\text{OH})_2$ instead of $\text{CaO} \cdot \text{H}_2\text{O}$, because the water can be relatively easily removed by drying, leaving the CaO in the gel. At D-drying this water is completely removed, as indicated by the chemical formula given. We visualize this molecule of water as interlayer water, whereas the 2 other molecules of water belong to the structure of the calcium silicate hydrate, possibly as indicated by our modification of Bernal's structural formula. Phosphorous pentoxide has smaller vapor pressure than D-drying, yet prolonged exposure of D-dried samples to P_2O_5 removed only a small percentage of the water.

D-drying removes all but a small part of the interlayer water. Usually, but not always, we obtained values a small percentage in excess of 2.0 molecules; longer drying would probably have removed this. Exposure to P_2O_5 removed this excess. The amount of adsorbed water was less than 0.01 mole per mole of SiO_2 (6).

The situation is very different at P-drying. The chemical formula of P-dried tobermorite gel having a CaO/SiO_2 ratio of 1.5 is $Ca_3Si_2O_7 \cdot 2.80H_2O$, and part of the extra 0.8 mole of water is interlayer water and part of it is adsorbed water. The two were determined in the following manner. Part of a hydrated C_3S paste was D-dried, and another part was P-dried. The same was done for a C_2S paste. The adsorption on the P-dried samples in the BET region of relative humidities was smaller than the adsorption on the D-dried samples. This was attributed to the fact that the P-dried samples contained some adsorbed water on their surfaces. The amount of adsorbed water was 0.26 mole; consequently, the other 0.54 mole was between the layers. The chemical formula of P-dried tobermorite gel was, therefore, $Ca_3Si_2O_7 \cdot 2.54H_2O$. The density of the gel indicated an average c -spacing of 10.2 Å, thus, clearly showing the presence of interlayer water. Furthermore, the P-dried samples, when immersed in water, very slowly in the course of days picked up some additional interlayer water, in contrast with the D-dried samples. The uptake was so slow that it was safe to assume that in the adsorption measurements on P-dried samples, which were performed at relative humidities of 0.07 to 0.33, no water went between the layers.

The value of 10.2 Å, obtained from the density measurements of P-dried pastes for the c -spacing, is obviously an average value. There is about half a mole of interlayer water per mole of gel, but the increase of approximately 1 Å in the c -spacing is not sufficient to accommodate water molecules. The explanation is that some of the tobermorite gel sheets do not contain interlayer water, but others do, which accounts for the average value obtained.

The main conclusions of this section are that there is practically no interlayer water in D-dried tobermorite gel, but there is a considerable amount of interlayer water in P-dried gel, probably about half of the maximum amount that can go between the layers. There is another important conclusion that can be drawn from these data. Even though the tobermorite gel could accommodate more than the 0.54 mole of water per mole of gel, which is between the layers in P-dried samples, 0.26 mole of water did not go between the layers but was attached to the surface. This illustrates the fact, long before known to us, that the combined water and the adsorbed water each have a spectrum of binding energies, and that the 2 spectra strongly overlap. The average binding energy of the interlayer water is greater than the average binding energy of the adsorbed water, but the most firmly bound part of the adsorbed water has a higher energy of binding than the most weakly bound part of the combined water. Thus, a separation of adsorbed and combined water on the basis of reversibility, as claimed in the new model, is impossible because the reversibility at a given humidity depends overwhelmingly on the binding energies.

These data, though conclusive by themselves, are not the only ones that show that there is very little or no interlayer water in D-dried cement pastes. One other set of experiments will now be cited (14), which by itself is as conclusive as the data given earlier. Table 1 gives data for pastes prepared from the same portland cement; w_0/c

TABLE 1
BET SURFACES, TOTAL POROSITIES, AND HYDRAULIC RADII OF PORTLAND
CEMENT PASTES

w_0/c	S_{H_2O} (m^2/g)	S_{N_2} (m^2/g)	$S_{H_2O} - S_{N_2}$ (m^2/g)	V_{H_2O} (ml/g)	V_{N_2} (ml/g)	$V_{H_2O} - V_{N_2}$ (ml/g)	r_{H_2O} (Å)	r_{N_2} (Å)	r_{in} (Å)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0.35	208.0	56.7	151.3	0.1264	0.0748	0.0516	6.1	13.2	3.4
0.40	202.6	79.4	123.2	0.1776	0.1059	0.0717	8.8	13.3	5.8
0.50	194.6	97.3	97.3	0.2615	0.1792	0.0823	13.4	18.4	8.5
0.57	193.8	132.2	61.6	0.3110	0.2493	0.0617	16.0	18.9	10.0
0.70	199.6	139.5	60.1	0.4008	0.2758	0.1250	20.1	19.8	20.8

is given in column 1. The pastes with $w_0/c = 0.35, 0.40,$ and 0.50 were hydrated for 12 years, the 2 others for $2\frac{1}{2}$ years. Columns 2 and 3 give the BET surface areas measured by water vapor and nitrogen adsorption, respectively, and column 4 gives the difference, i. e., the surface inaccessible to nitrogen. Columns 5 and 6 give the total porosities, measured by the adsorption of water vapor and nitrogen, respectively, and column 7 gives the difference, i. e., the pore space inaccessible to nitrogen.

The volume divided by the surface is called hydraulic radius. It is a measure of the average width of the pore system. If a pore is visualized as a cylinder, the hydraulic radius is one-half of the radius of the cylinder; and if a pore is assumed to be bounded by 2 parallel plates, the hydraulic radius is one-half of the distance between the plates. Columns 8, 9, and 10 give the hydraulic radii of the pore system accessible to water, that accessible to nitrogen, and that inaccessible to nitrogen respectively.

From the point of view of our discussion, column 10 has great significance. The hydraulic radius for the paste made with $w_0/c = 0.70$ shows that nitrogen cannot penetrate into very large pores. The smallest hydraulic radius, that obtained for the paste with $w_0/c = 0.35,$ is 3.4 \AA for the pores inaccessible to nitrogen. This is equivalent to a distance of 6.8 \AA between 2 parallel plates (or 2 layers); thus, even this value is much too large to be attributed to water occupying interlayer spaces.

The reason for the inability of nitrogen to penetrate into large pores is given in the paper (14). The pores have very narrow necks; they are what the surface chemists call "ink-bottle" pores. The difference between the penetrating abilities of nitrogen and water depends not only on the difference between the sizes of the molecules but also on 2 additional factors. The first is that a water molecule has a strong dipole, which is strongly attracted to the ionic surfaces of the compounds in hydrated cement, whereas the attraction for the nonpolar nitrogen is very much smaller. The second factor is concerned with rates. The constrictions in the necks of the pores present an energy barrier to the diffusion of the molecules into the pores. This is called activated diffusion. The barrier may be larger for nitrogen than for water because of the difference between the sizes of the molecules, but let us assume that the energy of activation is the same for both. Then, because of the temperature difference (298 versus 77 K), water should pass over the energy barrier 50 times as rapidly as nitrogen. Even for water, it takes 2 to 3 weeks to equilibrate; it would take as many years for nitrogen to equilibrate.

The phenomenon of activated diffusion in adsorption is well known to surface chemists. Maggs, for example, obtained much larger surface areas for a number of coals by butane adsorption than by nitrogen adsorption, in spite of the fact that butane has much larger molecules than nitrogen (15). The reason is that the nitrogen adsorption was measured at 77 and 90 K , whereas the butane adsorption was measured at 273 K . The nitrogen areas measured at 90 K were considerably higher than those measured at 77 K , which is also in line with the concept of activated diffusion through narrow entrances.

According to the Powers model, completely hydrated pastes of the same cement should have the same specific surface area, regardless of the initial water-cement ratio. The average of the values given in column 2 of Table 1 is $200 \text{ m}^2/\text{g}$. The maximum deviation from the mean is 4 percent. The nitrogen areas given in column 3 vary by almost a factor of 3. At $w_0/c = 0.35,$ the nitrogen area is 27 percent of the water area; it increases systematically with increasing w_0/c ratio, and at $w_0/c = 0.70$ it becomes 70 percent of the water area. In recent and as yet unpublished work, the nitrogen area for pastes made with $w_0/c = 0.2$ was less than $1 \text{ m}^2/\text{g}$ after 28 days of hydration, or much less than 1 percent of the water area. It was very interesting to find that the water surface area was considerably smaller after 28 days than after 7 days, even though the nonevaporable water indicated a considerable increase in the degree of hydration. The increase in hydration products resulted in the filling up of certain pores, or in making certain pores so narrow that even water could not penetrate into them.

Feldman and Sereda have cited the nuclear resonance studies of Seligmann (16) as a confirmation of their contention that most of the adsorbed water is interlayer water. The problem of interlayer water, we believe, is settled by the experiments discussed earlier, but now we will proceed to show that there is nothing in the work of Seligmann that invalidates our conclusions.

Seligmann's conclusions are based on T_2 , the transverse or spin-spin relaxation time, obtained from nuclear magnetic resonance measurements. Within the great insensitivity of the T_2 values to the state of binding of water, his results are not contradictory to ours.

Let us start with his ettringite samples, one equilibrated at a relative humidity of less than 1 percent (Sample 7), the other at about 50 percent (Sample 6). The T_2 values were 300 to 500 μsec for both. Seligmann concludes: "These results also demonstrate the previously mentioned lack of correlation between proton mobility and gross chemical properties; the escaping tendency of the water in Samples 6 and 7, as manifested by the equilibrium relative humidities of the samples, must be very different; yet the proton mobilities are of the same order of magnitude." The difference between the free energies of binding of water in Samples 6 and 7 is $RT \ln f_6/f_7$, which is 2,300 cal/mole, if the equilibrium humidity of Sample 7 is taken as 1 percent, and considerably more if the humidity is considerably less than 1 percent. Yet Seligmann, in spite of the quoted sentence, draws conclusions about the binding energies from proton mobilities.

One of the most puzzling aspects of Seligmann's paper is that he treats physically adsorbed water as though it were a definite entity, identical for the entire adsorption isotherm (with the exception of some active centers) and identical for different adsorbents. The heat of adsorption of water on anatase gradually decreases from 24,000 cal/mole to less than half of this value within the first adsorbed layer, and the heat of adsorption in the second layer is close to the heat of liquefaction, 10,000 cal/mole (17). The heats of adsorption of water on silica gel, tobermorite gel, and anatase are very different.

Seligmann obtained a T_2 value of about 2,300 μsec for a silica gel equilibrated at a relative humidity of 36 percent. This silica gel, on which the senior author of this paper and his co-workers did much work in the past and present, has an almost completely hydroxylated surface, plus (under the experimental condition of Seligmann) a complete, adsorbed monolayer of greatly differing energies of binding, plus a considerable amount of adsorbed water in the second layer. Seligmann states: "The present data indicate that water in only a single state is being observed." If the proton mobility has any correlation at all with binding energies, the "single state" observed in this instance is that of the most weakly adsorbed part of the water. The T_2 value is then taken by Seligmann as the standard for "physically adsorbed" water and is compared with water adsorbed on tobermorite gel.

Seligmann's C_3S paste (Sample 4) was D-dried and the T_2 value was about 200 μsec . About 40 percent of hydrated C_3S is calcium hydroxide, and the T_2 value for calcium hydroxide is 7 μsec . Thus, the proton in the hydroxyl does not show up, just as in the case of silica gel. There is no interlayer water in D-dried tobermorite gel, as was shown before; the 2 molecules of water are parts of the calcium silicate hydrate in the layers and not between the layers. Bernal's structural formula may be right or wrong; this has no bearing on the subject. The fact is that the 2 molecules of water are very strongly bound as was shown earlier.

Seligmann's alite paste (Sample 3) was equilibrated at a relative humidity of 16 percent. Under this condition, there is a good deal of interlayer water present, plus at least 1 layer of adsorbed water. Thus, there is much water present that is less strongly bound than in his C_3S paste, and this is shown in his T_2 value of 300 to 500 μsec . In the C_3S paste, all the water was strongly bound; in the alite paste, there was interlayer water plus about a monolayer of adsorbed water; and in silica gel, there was considerably more adsorbed water than a monolayer and, in addition, the energy of adsorption on silica gel is considerably smaller than on tobermorite gel. The binding energies up to this point, therefore, show at least a vague qualitative correlation with proton mobilities. However, the great insensitivity to binding energies shows up again in Samples 1 and 2. These are calcium silicate hydrates equilibrated at relative humidities of 70 and 50 percent respectively, and the T_2 values are still 300 to 500 μsec . Just as in the case of ettringite, the fugacities of the water in Samples 1, 2, and 3 are very different; consequently, the free energies of binding are also very different, but the mobilities of the protons, within the large experimental errors, are the same.

Seligmann's first conclusion is as follows: "Nuclear magnetic resonance results indicate that the state of binding of evaporable water in hardened cement paste up to 70 percent relative humidity is essentially the same as that of interlayer water in swelling clays or of water of crystallization in certain lattices." This statement, in the light of the earlier discussion, is unwarranted. The correct statement would replace "state of binding" with "mobility of protons," and would point out the great insensitivity of the results.

Seligmann's second conclusion is the following: "The water in calcium silicate hydrates equilibrated at or below 70 percent relative humidity has definitely less mobility than physically adsorbed water, but is still more mobile than chemically combined water in a crystal lattice." This statement should also be revised. Physical adsorption begins at 70 percent relative humidity only on very strongly hydrophobic surfaces. On the strongly hydrophilic surface of tobermorite gel, at 70 percent relative humidity the amount of adsorbed water corresponds to almost 3 monolayers. The calcium silicate hydrates at 70 percent relative humidity contain strongly bound water within the layers, plus interlayer water, plus almost 3 layers of adsorbed water on their surfaces. It is easy to accept that the mobility of the protons in the fourth and higher adsorbed layers is greater than that of the protons of any of the rest of the water.

Although we disagree with Seligmann's conclusions, we welcome his efforts, as well as those of others, to bring a new tool to the study of the states of water in hydrated cements. Nuclear magnetic studies, especially if their accuracy is improved, may throw new light on many problems in cement chemistry.

THE EXPERIMENTS OF FELDMAN AND SEREDA

The first statement that can be made about the pastes and compacts of Feldman and Sereda is that they were nowhere near to the D-dried state. The nonevaporable water, w_n , of 0.25 g/g of cement in Feldman's paper (12) and 0.254 g/g of cement in the paper of Soroka and Sereda (18), offered as the values for complete hydration, indicates that their quick-drying was approximately equivalent to P-drying. Likewise the value of Feldman for the water area (designated by him as the "conventional" water area), 165 m^2/g for complete hydration, indicates a drying equivalent to P-drying. The D-dried surface given in Table 1, column 2, is 200 m^2/g . The fact that they used a different cement from ours does not alter our conclusion. The variation in w_n and surface area for type 1 cements at complete hydration is slight.

We have shown that D-drying and P-drying lead to very different pastes. D-drying leaves neither interlayer water nor adsorbed water in the tobermorite gel; P-drying leaves both interlayer and adsorbed water in the gel. Thus, comparing the adsorption results of Feldman and Sereda with our results for D-dried pastes has no justification.

It is of interest to compare the properties of the bottle-hydrated and the paste-hydrated cement in Feldman's Table I (12). The values of w_n are 21.5 and 23.0 respectively indicating that the degree of hydration of the former is 93.5 percent of the latter. The nitrogen surfaces are 30 and 47 m^2/g ; the first of these values is 64 percent of the second. On the basis of this, it should have been concluded that the hydration products in bottle and paste hydration are different. However, the "conventional" water area comes to the author's help. The values are 142 and 152 m^2/g ; the former is exactly 93.5 percent of the latter. This phenomenal agreement, not mentioned by the author, indicates that the hydration products were actually the same. Nevertheless, even though the hydration products, which determine the surface area, and the true surface areas (those measured by water) were the same, there was a difference in pore structures. The ratio of nitrogen surface to water surface was 21 percent for the bottle-hydrated compact and 31 percent for the paste, a difference of almost 50 percent. This is a clear indication of the difference in pore structure. Pore structures strongly influence the adsorption properties of solids. Feldman (12) discusses the properties of the adsorption-desorption isotherms of his bottle-hydrated compacts, draws his conclusions on the basis of the discussion, and declares the validity of the conclusions for hydrated pastes. It is not clear to us why he did not discuss his pastes instead, if he wanted to draw conclusions about the pastes.

Feldman used a water-cement ratio of 0.5 for his pastes, and at 92 percent hydration he obtained a nitrogen area of $47 \text{ m}^2/\text{g}$. For complete hydration, the area would be $51 \text{ m}^2/\text{g}$. The nitrogen area, given in Table 1, column 3, of the present paper, is almost twice as great. We have already stated that the water area obtained by Feldman was approximately what one would expect for P-dried pastes, which is about 83 percent of the area of D-dried pastes. We have not investigated the nitrogen area of P-dried pastes, but Feldman's result indicates that the discrepancy between water and nitrogen area is much greater for these than for D-dried pastes. This can possibly be explained by assuming that the adsorbed water that is on the surface of P-dried pastes blocks the entrance of nitrogen into many pores.

One additional item in Feldman's paper is worth mentioning. Soroka and Sereda (18) determined the modulus of elasticity of the solid phase in hydrated portland cement. This involves an extrapolation to zero porosity. The porosities of the samples were calculated from the weight, volume, and degree of hydration, which is unquestionably a correct way of doing it. Although the authors do not mention it, these values are in good agreement with the porosities measured by water. The modulus of elasticity obtained by them was $88 \times 10^4 \text{ kg/cm}^2$, and they point out that this agrees "surprisingly well" with the results of Helmuth and Turk (19). The latter authors obtained values of 76×10^4 and $81 \times 10^4 \text{ kg/cm}^2$ for 2 cements by an entirely different method. Feldman, in his paper, simultaneously submitted with that of Soroka and Sereda, rejects the value obtained by his colleagues, and on the basis of the new model proposes a value that is less than half of their value.

The proponents of the new model question the validity of the BET surface area obtained by water on the ground that some of the water was irreversibly adsorbed; consequently, there was no thermodynamic equilibrium in the relative humidity range employed, 7 to 33 percent. We have already pointed out that no conclusion can be drawn from their results about D-dried pastes, but there is more to be said on the subject.

Thermodynamic reversibility with respect to pressure means that, if there is an infinitesimal change in pressure that changes the state of the system, the system returns to its original state if the pressure is restored to its original value. Because it is impossible to produce infinitesimal changes, we test for reversibility on a macro-scale. If a process is reversible with respect to a finite change in pressure, it is certainly a reversible process; but if it is not reversible within a certain time, it may still be reversible if adequate time is allowed for reversal. The adequate time may be days or months or years.

For the adsorption points in the BET region of relative humidities we allowed, on the average, about 3 weeks of equilibration for D-dried pastes. If the adsorption isotherm is determined up to saturation pressure, and a desorption isotherm is determined subsequently, much longer time is needed for equilibration. The energy of activation of desorption is equal to the energy of activation of adsorption plus the heat of adsorption. Because the heat of adsorption of water is high, the rate of desorption is much slower than the rate of adsorption. If one does not wait for weeks, one obtains an open hysteresis loop down to zero pressure. If one uses 1 day for equilibration of each point on the desorption curve, as Feldman did (12), one obtains a gigantic hysteresis loop. There is no point on his desorption isotherm (Table II) that comes anywhere near to equilibrium.

In contrast with this, Copeland waited for equilibration on the desorption side for weeks, and he obtained an isotherm in which the hysteresis loop closed around a relative humidity of 50 percent. This work was never published, but we can report here even more striking results, which will be published in the near future. Our co-worker, J. Hagymassy, determined adsorption-desorption isotherms for 9 pastes (3 C_3S , 3 C_2S , and 3 portland cement pastes). The w_0/solid ratios ranged from 0.4 to 0.7, and hydration times were several years, ranging up to 7 years. The pastes were D-dried. The desiccator method (20) was used, and different portions of the same paste were simultaneously exposed to different relative humidities, thus cutting down the time required for the isotherms from years to months. After $4\frac{1}{2}$ months of equilibration of the desorption points, they joined the adsorption isotherms at a relative humidity of about 60 percent, and the hysteresis loops were considerably smaller than those of Copeland.

These results show clearly that our adsorption isotherms represent equilibrium results, regardless of whether Feldman's do or do not. He allowed much longer times for the equilibration of the adsorption points than the desorption points; consequently, the adsorption isotherms may represent equilibria, or close to it. The agreement of the w_n and water surface area values with those obtained by us for P-dried pastes indicates that equilibrium may have been attained on the adsorption side.

We are not attempting to give a detailed explanation of the "loops" of the authors of the new model, by which they try to separate reversible and irreversible water. We have already pointed out that irreversible water may become reversible if the experimenter waits long enough for equilibration. It is possible that most of the loops, if not all, would have disappeared if months would have been allowed for equilibration. It was shown in the discussion of P-dried pastes that a considerable part of the adsorbed water is more strongly bound than much of the interlayer water. The heat of adsorption of water is high; it is highest at the lowest humidities; consequently, the rate of desorption is very slow. Instead of separating reversible and irreversible water, Feldman and Sereda separated reversible and less reversible water. Hydrated cement has a variety of compounds in it, with water of hydration of different binding energies and with a spectrum of binding energies of adsorbed water; thus, their method of separation of reversible and irreversible water and their identification with adsorbed and interlayer water are unacceptable to us.

The researches of Sereda and his co-workers contain a large amount of valuable experimental work on hydrated portland cements. These results, if properly interpreted, can throw additional light on the structure of portland cement paste and concrete. We do not mean to imply that all of their own interpretations are erroneous; many of these have nothing to do with their new model or are even contradictory to it. An example of this was already cited in the paper of Soroka and Sereda (18). We do not mean to imply, either, that the Powers model is complete. We do mean to state, however, that the Powers model, as modified and extended by many of us, explains quantitatively many and semiquantitatively many other aspects of the structure of paste, and that we know of no properly interpreted experimental evidence to date that contradicts it.

Feldman and Sereda have offered an explanation of the hysteresis, which is based on the entrance and exit of interlayer water. The explanation is ingenious, and for the kind of hysteresis that is caused by interlayer water it may be correct. P-dried pastes contain interlayer water, and in the long extended adsorption runs of Feldman and Sereda additional water was likely to go between the layers, part of which probably comes out in the desorption run. However, adsorbed water itself also shows hysteresis; in fact, all adsorbates show hysteresis for practically all porous adsorbents. Nitrogen, which certainly does not enter into the interlayer spaces of hydrated cements, silicates, clay minerals, and other layer crystals, shows hysteresis for these and most other porous bodies. Examples of these for portland cements are given in a paper already cited (14), and the literature of adsorption contains hundreds of other examples for a great variety of adsorbent-adsorbate systems. The oldest theory of the hysteresis in adsorption was proposed by Zsigmondy 58 years ago (21), and several other theories have been proposed since (22). Although the theory of Feldman and Sereda can explain only a part of the hysteresis in their own adsorption-desorption data, it may be added to the other theories as a plausible explanation of a special type of hysteresis encountered in the study of layer crystals.

THE STRENGTH OF CEMENT PASTE

In the Powers model, as well as in all of its modifications and extensions, the cementing material is the cement gel, which is essentially tobermorite gel, though it probably does contain small amounts of other constituents besides the calcium silicate hydrate. One statement of our view on the cause of strength is as follows (23):

The adhesive forces, which are responsible for strength, are primarily van der Waals forces, but there may also be some chemical binding involved. Tobermorite gel is a "limited swelling" gel—although it swells slightly in water, it is not dispersed as, for example, gelatin. A possible explanation for this is that the gel particles are bound to each other at certain points by chemical

valence forces. The low tensile strengths of hardened paste and concrete, however, indicate that the chemically bound contact points cannot be very numerous. The tensile strength is only about one-tenth of the compressive strength, and if chemical binding would play an important role in the adhesion of the gel particles, one would expect that much greater force would be needed to pull them apart.

Sereda and his co-workers seem to disagree with these statements, though it seems to us that there is no disagreement at all. Soroka and Sereda state (18): ". . . the chemical bonds, if present in the paste, play an insignificant role." This is in agreement with our statement. Both state that there may or may not be any chemical bonds present; if they are present, they play a minor role in producing strength. For the rest, Sereda and his co-workers attribute the strength to "interparticle bonds." This is a singularly unfortunate name, because it is the interparticle bonds that are to be explained by the nature of the forces producing them. On the basis of their description of the interparticle bonds, it seems to us that they are talking about van der Waal's forces, though they refrain from using, or even seem to be opposed to, this name. If they are talking about other than van der Waal's forces, they must have some force in mind that is unknown to the present authors.

The old and the new model are in complete agreement on a point of overriding importance: that the most important cementing and strength-producing material in hardened paste and concrete is the tobermorite gel. Recently, however, an idea has been put forward by Williamson (24), which at first glance appears to be surprising, but on closer inspection it can be brought into line with our ideas.

In the abstract of his paper, Williamson states: "The originally water-filled space between the grains is partially filled with calcium hydroxide crystals that appear to be responsible for the strength of cement paste." A much weaker statement is in the text: ". . . the ultimate strength of portland cement paste is related to the $\text{Ca}(\text{OH})_2$ that fills the originally water-filled space." We shall now examine what sort of calcium hydroxide Williamson is talking about. According to him in hydrated C_3S , ". . . the outer product can vary from an almost pure $\text{Ca}(\text{OH})_2$ to a calcium silicate hydrate based on a two-phase structure of SiO_2 and $\text{Ca}(\text{OH})_2$."

Williamson's arguments for the "two-phase structure" of tobermorite gel (25) have little or no bearing on the subject. It seems from his description of the structure of the calcium silicate hydrate that the $\text{Ca}(\text{OH})_2$ and the SiO_2 form a single structure of variable composition, which is known and accepted by everybody. Nevertheless, there are 2 types of calcium hydroxide in hydrated C_3S . There are large calcium hydroxide crystals, part of them visible in an ordinary microscope, and there is calcium hydroxide in the tobermorite gel. We have already cited Brunauer's somewhat flamboyant statement that tobermorite gel is a "chemical mixture" of calcium hydroxide and hydrous silica.

The calcium hydroxide crystals may or may not have cementing or strength-producing properties. Williamson himself shows in his Figure 1 (25) that C_3S and C_2S hydrated for 1 year have the same compressive strength. Actually there are results that show greater strength for the C_2S paste than for the C_3S paste after 2 years of hydration. This is in spite of the fact that the C_2S paste contains much less calcium hydroxide than the C_3S paste. One of the present authors (Ivan Odler) made numerous experiments on the reaction of portland cement with pozzolanic materials and with sand in mortars at room temperatures. The sand was ground to have the same fineness as the pozzolanic materials. The sand did not react with the calcium hydroxide in the cement, but some of the pozzolanic materials did, and in fact removed the calcium hydroxide almost completely. These mortars had considerably higher strengths than the sand mortars because of the formation of additional calcium silicate hydrate.

The situation is very different with the lime within the tobermorite gel. Gard, Howison, and Taylor have suggested that the lime in tobermorite gel is responsible for cementing neighboring gel particles together (26). Kantro, Brunauer, and Weise went a step further, and suggested that lime cements the layers within the gel sheets to each other (20).

The cementing action by van der Waal's forces, the bonds between the surfaces, and the strength of the material depend on surface energy and specific surface area. Cal-

cium hydroxide has a high surface energy, but just because of this it has a low surface area. Silica (especially in the form of silica gel) has a very low surface energy, but just because of this it has a very high area. The function of the silica in tobermorite gel is possibly to spread out the lime, to give it a high surface. At any rate, tobermorite gel has high surface area combined with a relatively high surface energy.

None of these arguments shows that calcium hydroxide crystals have no cementing action. They only show that the calcium silicate hydrate is a better cementing agent than calcium hydroxide. It is possible that calcium hydroxide does play a role in cementing, but only future research can settle whether it plays a significant role.

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REFERENCES

1. Feldman, R. F., and Sereda, P. J. A Model for Hydrated Portland Cement as Deduced From Sorption—Length Change and Mechanical Properties. *Materiaux et Constructions*, Vol. 1, No. 6, 1968, pp. 509-520.
2. Powers, T. C., and Brownyard, T. L. Studies of the Physical Properties of Hardened Portland Cement Paste. *ACI Jour.*, Proc. Vol. 43, Oct. 1946, p. 101; Nov. 1946, p. 249; Dec. 1946, p. 469; Jan. 1947, p. 549; Feb. 1947, p. 669; March 1947, p. 845; April 1947, p. 933.
3. Brunauer, S., Emmett, P. H., and Teller, E. Adsorption of Gases in Multimolecular Layers. *Jour. of Am. Chem. Soc.*, Vol. 60, 1938, pp. 309-319.
4. Brunauer, S., Kantro, D. L., and Weise, C. H. The Surface Energy of Tobermorite. *Canadian Jour. of Chem.*, Vol. 37, 1959, pp. 714-724.
5. Born, M., and Stern, O. *Sitz. Ber. Preuss. Akad. Wiss.*, 1919, p. 901.
6. Brunauer, S., Kantro, D. L., and Copeland, L. E. The Stoichiometry of the Hydration of β -dicalcium Silicate and Tricalcium Silicate at Room Temperature. *Jour. of Am. Chem. Soc.*, Vol. 80, 1958, pp. 761-767.
7. Brunauer, S., Kantro, D. L., and Weise, C. H. The Surface Energies of Calcium Oxide and Calcium Hydroxide. *Canadian Jour. of Chem.*, Vol. 34, 1956, pp. 729-742.
8. Brunauer, S., Kantro, D. L., and Weise, C. H. The Surface Energies of Amorphous Silica and Hydrous Amorphous Silica. *Canadian Jour. of Chem.*, Vol. 34, 1956, pp. 1483-1496.
9. Kantro, D. L., Weise, C. H., and Brunauer, S. Paste Hydration of Beta-Dicalcium Silicate, Tricalcium Silicate, and Alite. *HRB Spec. Rept. 90*, 1966, pp. 309-327.
10. Wittmann, F. *Materiaux et Constructions*, Vol. 1, 1968, p. 547.
11. Kantro, D. L., Brunauer, S., and Weise, C. H. Development of Surface in the Hydration of Calcium Silicates. II. Extensions of Investigations to Earlier and Later Stages of Hydration. *Jour. of Phys. Chem.*, Vol. 66, No. 10, 1962, pp. 1804-1809.
12. Feldman, R. F. Sorption and Length Change Scanning Isotherms of Methanol and Water on Hydrated Portland Cement. *Fifth Internat. Symposium on the Chemistry of Cement*, Tokyo, Paper III-23, 1968.
13. Bernal, J. D. *Proc. Third Internat. Symposium on the Chemistry of Cement*. London, 1952, p. 216.
14. Mikhail, R. Sh., Copeland, L. E., and Brunauer, S. Pore Structures and Surface Areas of Hardened Portland Cement Pastes by Nitrogen Adsorption. *Canadian Jour. of Chem.*, Vol. 42, 1964, pp. 426-438.
15. Maggs, F. A. P. *Nature*, Vol. 169, 1952, pp. 259, 793.
16. Seligmann, P. Nuclear Magnetic Resonance Studies of the Water in Hardened Cement Paste. *Jour. of PCA Research and Dev. Laboratories*, Vol. 10, No. 1, 1968, pp. 52-65.

17. Harkins, W. D., and Jura, G. Jour. of Am. Chem. Soc., Vol. 66, 1944, p. 919.
18. Soroka, I., and Sereda, P. J. The Structure of Cement-Stone and the Use of Compacts as Structural Models. Fifth Internat. Symposium on the Chemistry of Cement, Tokyo, Paper III-34, 1968.
19. Helmuth, R. A., and Turk, D. H. Elastic Moduli of Hardened Portland Cement and Tricalcium Silicate Pastes: Effect of Porosity. HRB Spec. Rept. 90, 1966, pp. 135-144.
20. Kantro, D. L., Brunauer, S., and Weise, C. H. Development of Surface in the Hydration of Calcium Silicates. In Solid Surfaces and the Gas Solid Interfaces, Advances in Chemistry Series, Vol. 33, 1961, pp. 199-219.
21. Zsigmondy, R. Z. anorg. allgem. Chem., Vol. 71, 1911, p. 356.
22. Brunauer, S., Mikhail, R. Sh., and Bodor, E. E. Jour. of Colloid and Interface Sci., Vol. 25, 1967, p. 353.
23. Brunauer, S. Proc. Eighth Conference on the Silicate Industry, Budapest, 1965, p. 205.
24. Williamson, R. B. Science, Vol. 164, 1969, p. 549.
25. Williamson, R. B. Jour. of Crystal Growth, Vol. 3-4, 1968, p. 787.
26. Gard, J. A., Howison, J. W., and Taylor, H. F. W. Synthetic Compounds Related to Tobermorite: An Electron-Microscope, X-Ray and Dehydration Study. Mag. of Concrete Research, Vol. 11, No. 33, 1959, pp. 151-158.

Discussion

R. F. FELDMAN and P. J. SEREDA, Division of Building Research, National Research Council of Canada—The authors discuss the new model at considerable length and compare it critically with the Powers model. We wish to take issue with the authors on many points. Because we are constrained by the rules on length of discussion, we can do little more than to provide a general reply in which the points in question are stated with limited supporting argument. We intend to prepare a further discussion later of the new model, with additional evidence that we hope may be acceptable as a paper in its own right.

The new model was intended to describe the average chemical, physical, and mechanical properties of hardened portland cement paste and, as such, must not be, and is not in our view, in serious conflict with available experimental evidence. We do not believe that the authors have adequately incorporated into their considerations evidence from our measurement of mechanical and physical properties (1).

We do not accept the proposition that data presented by Feldman (12) can be disregarded because they were obtained under the "wrong" conditions, i. e., that the samples were held not to have been in equilibrium as stated or they were held to have been incorrectly dried. It is our opinion that these adsorption isotherm data are valid, that they agree with other published data, and that they provide further evidence in support of the new model. We believe that the evidence adequately supports the following conclusions:

1. Interlayer water can reenter D-dried material, even at low humidities;
2. In light of this conclusion, water surface areas and densities are not correct and the respective nitrogen or methanol values are approximately correct; and
3. The fundamental physical properties of the hydrated calcium silicates, such as density, Ca-Si ratio, H₂O-Si ratio, surface area, and distance between layers, vary with conditions of preparation.

We offer further comments as follows:

The authors consider that their measurement of surface energy yields results of major importance. This technique requires that the samples used are of constant composition and are the same in every way except for the quantitative difference in surface

area. However, if C-S-H is a family of ill-defined, poorly crystallized, layered materials possessing various proportions of both internal and external area, this requirement is not met. In the experiments, the samples were prepared by vastly different methods and from different starting materials. As a result, it may be proposed that the ratio of internal and external areas changed with preparation as well as Ca-Si ratio, density, interlayer spacing, and H₂O-Si ratio.

Thus, one is led to the conclusion that measurements on a group of such samples, varying in so many ways, would not meet the requirements of the surface energy method. Thus, we suggest, apparent surface energy values must be looked upon as subject to large uncertainty and should not be regarded as adequate evidence to support the contention that water surface areas are correct.

The acceptance of the water surface area evidence (6) necessarily implies acceptance of the results of density measurements of cement paste by water immersion that yield values in the order of 2.86 g/cm³. This is very much higher than density measurements obtained by helium pycnometry that are as low as 2.33 g/cm³ for D-dried specimens prepared at a w-c ratio of 0.8.

If a calculation of interlayer spacing from density is meaningful, one obtains a value of 11.4 Å instead of 9.3 Å as reported by Brunauer et al. (6).

The authors devote much space to the discussion of interlayer water and conclude that water does not reenter the interlayer spaces. This conclusion is in direct conflict to much evidence of workers in the USSR (27), Mikhail (29), Powers (2), Helmuth (29), and Feldman (12). No isotherms of cement or paste-hydrated C₃S showing closed loops have been published to our knowledge. In discussing isotherms published by Feldman, the authors conclude that the samples were not adequately D-dried or were not in equilibrium, and propose that weeks, months, or even years may be required for the attainment of equilibrium. In contrast the accepted method for D-drying as developed by Copeland and Hayes (30) involves 4 to 7 days of equilibration with a vapor pressure corresponding to ice at -79 C. This drying includes removing all the strongly held first layers of adsorbed water plus removal of the more tightly held interlayer water. In point of fact, there are many pieces of evidence that favor our contention that the samples used by Feldman were in equilibrium throughout the isotherm and were D-dried.

One of the major points of conflict arises over the question of whether the interlayer water removed on D-drying can subsequently reenter the interlayer spaces. In their attempt to prove that this is so, the authors have calculated the hydraulic radius of the pores from data obtained from adsorption of water and of nitrogen. Their results show that the values of hydraulic radius were too large to be attributed to water occupying interlayer spaces. Logically, this calculation is incorrect in that SH₂O - SN₂ (Table 1, column 4), used as a measure of internal surface area, should really have been calculated from 755 - SN₂, i. e., the difference between the nitrogen surface area (external) and the total surface area, including the interlayer surface, implied by the model. If the calculation is made from this premise, the average value of the calculated hydraulic radius that results is 1.32 Å, almost the same as that which could be obtained for a montmorillonite clay, 1.26 Å. Thus, the properly calculated hydraulic radius is entirely compatible with water occupying interlayer spaces.

In discussing strength of the cement paste, the authors noted the apparent agreement between the 2 models with regard to the role of chemical bonds in producing strength. We do not believe they have adequately taken into account the ideas developed by Soroka and Sereda (18) regarding the "interparticle bonds"—an expression used by Powers in developing his model. This was an attempt by both Powers and Soroka and Sereda to define the nature of the interparticle boundary.

The 2 models are actually not in agreement on this point. The Powers model postulates that interparticle distance or boundary varies and considers the existence of wedge-shaped crevices into which adsorbed water enters and alters the interparticle attraction and hence interparticle distance, thus accounting for most of the dimensional changes. We postulate that adsorbed water as such plays no part in the interparticle bond although the interlayer water may contribute where the boundary is similar to that between layers.

References

27. Luk'yanova, O. I., and Rebinder, P. A. Properties of Tobermorite-Like Hydro-silicates as a Variable Composition Phase. *Doklady Akademii Nauk SSSR*, Vol. 184, 1969, pp. 1144-1147.
28. Mikhail, R. Sh., Kamel, A. M., and Abo-el-enein, S. A. Surface Properties of Cement Hydration Products. I. Pore Structure of Calcium Silicate Hydrates Prepared in a Suspension Form. *Jour. Appl. Chem.*, Vol. 19, 1969, pp. 324-328.
29. Helmuth, R. A. Private communication.
30. Copeland, L. E., and Hayes, J. C. The Determination of Nonevaporable Water in Hardened Portland Cement Paste. *ASTM Bull.* 194, 1953, p. 70.

PAUL SELIGMANN, *Portland Cement Association*—The present writer welcomes the authors' discussion of the nuclear magnetic resonance (NMR) results (16) and also the opportunity to clarify some matters that appear to have caused confusion. For this purpose it is necessary first to make some general comments on the nature of the NMR phenomenon and on the terminology used in the paper.

The major source of confusion relates to the energy of the water molecules. At no point in the original paper (16) was the use of the terms "state" or "binding" intended to refer to the energy or heat adsorption. The energies associated with nuclear resonance effects are those required to change the axis of rotation of a proton, not those required to remove a water molecule from a particular state of binding. These energies are readily calculated. At the frequency, $\nu = 7.3 \times 10^6$ Hz used in the wide line work of Plaine (31), the energy absorbed by a single proton is $h\nu$, where h is Planck's constant. This energy corresponds, in heat units, to 1.4×10^{-3} g-cal/mole of water, an exceedingly small fraction of the energy of adsorption. An observed line width then corresponds to a small range of resonance energies around this value. It must be understood that NMR measures parameters of the system other than the energy of adsorption.

The use of a magnetic field to separate different atomic or molecular states having the same energy is by no means new. This technique has, for example, been widely used in the field of atomic emission spectroscopy, where it is known as Zeeman effect, for more than half a century. A single atomic energy level is split into a number of closely spaced levels whose separation depends on the strength of the applied magnetic field. In this context, NMR is the same technique applied to nuclear absorption spectroscopy rather than atomic emission spectroscopy. In both cases, fine details of a system are determined from small energy perturbations.

NMR can be compared with a much older type of radio frequency absorption spectroscopy, the measurement of dielectric constant. In that technique, the measured absorption of radiation depends on the ability of the various dipoles to "follow" the field. In the case of NMR, the absorption measures the ability of the protons to shift their spin axes in accordance with an impressed alternating component of the local magnetic field. This local field is very complex (16). The parameter, T_2 , that is measured is a relaxation time associated specifically with the local field variations caused by the rotations of spin axes of neighboring protons and has been found to vary with the state of the water, as indicated in the paper (16). T_2 thus measures the degree of restraint of the immediate environment on the spin axis of the proton. A proton that is not free to reorient its spin axis must be in a restrained or bound state; it is in this sense that the term "binding" was used in the paper.

A major result from the transient equipment, apparently overlooked by the authors, was the absence of echoes in the pulsed NMR of the pastes up to 70 percent relative humidity, as contrasted with the presence of echoes for the silica gel at a much lower relative humidity. In fact, Zimmerman and his co-workers (32) reported proton spin echoes from a silica gel covered with less than 0.05 layer of water. The absence of echoes from pastes means that even the most mobile of the protons are in a state of

restraint that is qualitatively different from that of even the protons in 0.05 layer of water adsorbed on silica gel. This difference is reflected in the "insensitivity" of the T_2 values, which stems from the poorly defined free induction decay signals obtained from pastes, as compared with the excellent echoes obtained by many workers from various silica gels and from the many other materials of high surface area discussed in the Winkler review (33). For silica gels, only those with very small pores, as studied by Tul'bovich and co-workers (34) exhibit a low proton mobility comparable with that found in cement pastes equilibrated up to 70 percent relative humidity.

Additional confusion has arisen with regard to the use of the terminology "physically adsorbed water." The classification of types of water used in the paper (16) is that of Powers and Brownyard (2). It was necessary in addition, however, to distinguish between types of physically adsorbed water as regards T_2 values and the ability to produce echoes. "Physically adsorbed water" was therefore arbitrarily used to denote the adsorbate of silica gel and similar materials, because of the wide use of water on silica gel as a classic example of physical adsorption. The interlayer water of swelling clays was used as an example of an adsorbate with low T_2 values and no capability for echo production.

It must be noted that "interlayer" refers here to a type of physical adsorption rather than chemical adsorption as is implied by the authors' model of the tobermorite formula and unit cell. The energy of adsorption for water in swelling clays is known to be in the range normally associated with physical adsorption (35). The wide difference between the surface areas measured by nitrogen and water adsorption on swelling clays has prompted some workers to speak of "external" and "internal" surface areas (36), where the latter refers to the interlayer area that can also be measured by adsorption of large organic molecules such as glycerin and ethylene glycol. All these facts, together with the unlimited swelling of the clays, indicate the water adsorption to be physical. Yet the T_2 values obtained are distinctly different from those of the water on materials like silica gel.

No model was proposed (16) to "explain" the results of the NMR measurements. Cement pastes differ from swelling clays not only in limited swelling capacity but also in the absence of X-ray diffraction lines for a definite c -spacing for the silicate phase (37), as would be characteristic of a layered structure. Any satisfactory model would have to account for the apparent surface area, the proton mobility, and also the degree of disorganization implied by the observed diffraction patterns. It is felt that this problem must be approached with great caution.

The present writer is optimistic about the improvement of experimental NMR techniques. There are now indications that new types of equipment and new ways of using presently available equipment for the study of solid materials are being developed. The absence of proton spin echoes dashed his original hopes of determining the complete proton mobility spectrum of cement paste as had been done by others for materials of high surface area. It is hoped that the new developments will still make this possible.

References

31. Blaine, R. L. Proton Magnetic Resonance in Hydrated Portland Cements. Proc. Fourth Internat. Symposium on the Chemistry of Cement, Washington, D. C., 1960, Vol. 1, Paper IV-S5, pp. 501-511; National Bureau of Standards, Monograph 43, 1962.
32. Zimmerman, J. R., Holmes, B. G., and Lasater, J. A. A Study of Adsorbed Water on Silica Gel by Nuclear Resonance Techniques. Jour. of Physical Chemistry, Vol. 60, Sept. 1956, pp. 1157-1161.
33. Winkler, H. Examination of Adsorption Phenomena by Nuclear Induction Methods. Archives des Sciences, Vol. 14, Sept. 1961, pp. 219-243.
34. Tul'bovich, B. I., Slisarenko, F. A., Klyayev, V. I., and Sorokin, S. I. Proton Magnetic Resonance of Water and Normal Hydrocarbons Sorbed by Silicate Sorbents of Various Pore Structure. Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya, Vol. 9, No. 5, 1966, pp. 735-737.

35. Mooney, R. W., Keenan, A. G., and Wood, L. A. Adsorption of Water Vapor by Montmorillonite. I. Heat of Desorption and Application of the BET Theory. *Jour. of Am. Chem. Soc.*, Vol. 74, 1952, pp. 1367-1371.
36. Diamond, S., and Kinter, E. B. Surface Areas of Clay Minerals as Derived From Measurements of Glycerol Retention. *Proc. Fifth National Conference on Clay and Clay Minerals*, 1958, pp. 318-333.
37. Copeland, L. E., and Kantro, D. L. Chemistry of Hydration of Portland Cement at Ordinary Temperature. *In The Chemistry of Cements* (Taylor, H. F. W., ed.), Vol. 1, New York Academic Press, 1964, p. 336.

STEPHEN BRUNAUER, IVAN ODLER, and MARVIN YUDENFREUND, *Closure*—First the discussion of Feldman and Sereda will be answered. The strongest argument in our paper, that based on the surface energy of tobermorite gel, is simply swept aside by the discussors. After making a wrong statement about the requirements of the technique of surface energy determinations, they point out that the samples had different lime-silica and water-silica ratios, but they fail to state that corrections were made for this. The surface energy values given in our paper refer to tobermorite gel of the composition $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. They point out as an objection that "the samples were prepared by vastly different methods and from different starting materials," and they fail to see that this is an argument for and not against the correctness of the surface energy of tobermorite gel. The fact that the plot of heat of solution versus surface area fell on the same straight line for these different samples and the fact that the slope of the straight line gave the theoretically correct surface energy value are not explained by the discussors.

The tobermorite gel obtained in the hydration of C_3S and C_2S is very poorly crystallized; its X-ray diffraction pattern consists of only 3 lines. Besides the 2 determinations of the surface energy discussed in the paper, Kantro, Brunauer, and Weise (38) also determined the surface energy of completely amorphous tobermorite gel, and its value fell between the 2 values given in the paper.

The discussors point out that we have not adequately incorporated evidence from their measurements of mechanical and physical properties. This is true; the only item that we have pointed out along these lines was the rejection by Feldman of the modulus of elasticity value of Soroka and Sereda, which was in agreement with the old model, based on water vapor adsorption. Our aim in the paper was to examine the bases of the 2 models: of the old model, based on water vapor adsorption data, and of the new model, based on nitrogen adsorption data.

Because nitrogen enters a part of the pore space, it is possible that some properties of the pastes can be correlated with nitrogen adsorption. It is, therefore, not enough to show such correlations; the discussors must show that their results cannot be correlated with the old model.

We would very much prefer if the phrase "D-drying" would be used only for the method of drying first used by Copeland, and widely used by us in our research. As far as we know, this method was never used by Sereda and his co-workers; so we will call their method F-S-drying. In our paper, on the basis of w_n and the surface area measured by water, we concluded that F-S drying is about the equivalent of P-drying. On the basis of the density value of 2.33 g/cm^3 , obtained by helium pycnometry, it appears that the samples of the discussors were less strongly dried than P-drying. The interlayer spacing calculated for D-dried samples was 9.3 \AA , for P-dried samples 10.2 \AA , and for F-S-dried samples 11.4 \AA .

If we can agree on semantics, and the discussors will stop calling their samples D-dried samples, a part of the disagreement will disappear. It is pointed out in our paper that water can enter the interlayer spaces of P-dried samples; in view of the previous paragraph, water should be able to enter even more easily into the interlayer spaces of F-S-dried samples. The statement in the discussion that we "conclude that water does not reenter the interlayer spaces" is completely erroneous; we have made this

statement only about D-dried tobermorite gel, and not about P-dried or F-S-dried samples. The references cited to refute a statement we have not made have no pertinence to the subject.

Although the w_n values of Feldman and Sereda were about equal to those of our P-dried samples, this does not mean that their samples and our samples were in the same state. The quick F-S-drying, even if it removes as much water as D-drying, or more water, cannot be compared to our slow drying, in which equilibrium or near equilibrium state of the system is reached.

The reiteration of the statement that desorption equilibrium with water vapor can be established in 1 day, in spite of our paper, is beyond our understanding. The discussors point out that D-drying as developed by Copeland produces equilibration with water vapor in 4 to 7 days. They fail to point out that the equilibration is accomplished at a vapor pressure that is between 4 and 5 orders of magnitude lower than theirs. If at such low vapor pressure 4 to 7 days are needed for equilibration, how can their desorption equilibrium be established in 1 day? Furthermore, Copeland used what we later called "soft drying," i. e., drying until the water loss was 1 mg per g of paste per day. Later we adopted "hard drying," i. e., drying to a water loss of 0.1 mg per g of paste per day, and this took 2 to 3 weeks.

As far as the adsorption isotherms of the discussors are concerned, our paper states that "the adsorption isotherms may represent equilibria or close to it." But the arguments of Feldman and Sereda are based on desorption not on adsorption, and their desorption points were very far from equilibrium.

The discussors state, "No isotherms of cement or paste-hydrated C_3S showing closed loops have been published to our knowledge." We do not know of any such published work either. However, our paper cites unpublished work by Copeland and by Hagymassy. The latter work, which will be published soon, will show not only closed hysteresis loops, but very small ones; in fact, for portland cement the hysteresis loops are hardly noticeable.

The discussors state that our calculations of the hydraulic radius of the spaces into which nitrogen cannot enter is logically incorrect. Our calculations are completely correct logically, if water measures the total pore surface and total pore volume of the paste, and this is shown in the paper. However, it is of interest to point out the errors in the thinking and calculations of the discussors. In the first place, $755 \text{ m}^2/\text{g}$ is the total geometric surface of tobermorite gel and not of hydrated portland cement. Less than half of the fully hydrated cement is tobermorite gel, so we will call the geometric surface $377 \text{ m}^2/\text{g}$. Let us see what results one gets on the basis of the new model. For the paste with $w_0/c = 0.35$, the surface inaccessible to nitrogen is $377 - 57 = 320 \text{ m}^2/\text{g}$. According to the new model, there is at least 1 layer of water between the tobermorite gel layers after D-drying. We will conservatively estimate the thickness of the water molecules as 2.1 \AA , which happens to be the difference between the c-spacings of F-S-dried samples, 11.4 \AA , and D-dried samples, 9.3 \AA . "Logical consistency" requires that if we consider the entire geometric surface as pore surface, we should also consider the entire geometric volume as pore volume. The volume occupied by interlayer water after D-drying, according to the new model, is $0.5 \times 377 \times 10^4 \times 2.1 \times 10^{-8} = 0.0396 \text{ ml}$. In addition to this, 0.1264 ml of water entered the pore system during adsorption up to saturation pressure. Thus, the total pore volume is 0.1660 ml per g of paste, and the pore volume inaccessible to nitrogen is 0.0912 ml . The hydraulic radius of the pore system inaccessible to nitrogen, thus calculated, is 2.9 \AA . If the pores are visualized as parallel plates, the hydraulic radius gives an average distance of 5.8 \AA between the plates; if the pores are cylindrical, the diameter of the average pore is 11.6 \AA ; and if the pores are spherical, the diameter of the average pore is 17.4 \AA . It is pores of such sizes into which nitrogen, with a diameter of 3.5 \AA , cannot penetrate, if the calculation is based on the new model. Because the dimensions given are average dimensions, many of the pores are naturally larger than the average.

In this calculation, everything was loaded in favor of the new model: The paste with smallest pores was selected; only one layer of water was assumed to be between the gel layers; and the thickness of the water molecules was assumed to be the smallest

possible thickness. Similar calculations for the paste with $w_0/c = 0.70$ give a hydraulic radius of 6.9 Å for the pores inaccessible to nitrogen; so the average distance between parallel plates is 13.8 Å, the average cylindrical diameter is 27.6 Å, and the average spherical diameter is 41.4 Å. These calculations show the logical inconsistency of the new model much better than the data given in Table 1. We should not forget, however, that these calculations are based on the wrong premises of the new model, and that the correct and logical values are those given in Table 1.

We are very grateful to Seligmann for his clear and logical discussion. It illustrates the difference between the thinking processes of physicists and chemists; when we chemists talk about "state" or "binding," we think about the energy of binding of water molecules to the surface, and the state of these molecules in the adsorbed phase. If we understand the discussion fully, our conclusion is that there is no contradiction between Seligmann's results and the old model; thus, his results cannot be cited in favor of the new model, as was done by Feldman and Sereda. We have stated in the paper that the Powers model, as modified by many of us, is not complete, and we expect that the time will come when the model will account even for such things as proton mobility.

Reference

38. Kantro, D. L., Brunauer, S., and Weise, C. H. The Ball-Mill Hydration of Tricalcium Silicate at Room Temperature. *Jour. of Colloid Science*, Vol. 14, 1959, pp. 363-376.