This paper deals with the interaction of water and solid in the Powers model of hardened cement paste. Experimental work is presented in three sections: (a) observation of shrinkage, swelling and gain or loss of moisture for specimens brought to equilibrium at various values of the ambient relative humidity; (b) direct measurement of swelling pressure; and (c) variation of cube strength with the quantity of evaporable water.

The results support the view that shrinkage strains may, on the first desorption cycle, be represented by a discontinuous function of hydrostatic stress calculated by means of the Kelvin equation. The function consists of two nearly linear portions; one appears to be associated with the action of film pressure together with hydrostatic tension, and the other with film pressure alone.

At the start of drying the shrinkage is predominantly due to hydrostatic tension which, according to Powers (2), is effective over the whole surface area of the solid. As the equilibrium relative humidity in the pores is reduced below about 45 percent, the hydrostatic tension exceeds the fracture strength of water and further shrinkage is associated with diminution of film pressure and elastic recovery of the solid. Different areas of the solid are acted upon by hydrostatic tension and film pressure. The reverse process on adsorption is not so clearly defined and this is explained by postulating the clustering of water molecules before formation of menisci.

The functions relating swelling and shrinkage strains with change in surface energy calculated according to the Gibbs equation are generally sigmoidal in shape, but are nearly linear on adsorption from the oven dry condition. Deviation from linearity in these relationships is tentatively ascribed to the complicating effects of menisci formation, movement of interlayer water, variation of the BET surface area, and hydration of cement during the course of the test. Values of the elastic modulus of primary particles of solid estimated from the analogous stress-strain curves were of the same order as values obtained elsewhere for porous glass and hard quartzite.

The external mechanical force necessary to prevent swelling was measured and equated to the stress in pore water calculated according to the Kelvin equation multiplied by an "effective area" factor. The effective area was about 2.5 percent of the area of the gross cross section at the stage of formation of menisci and increased to nearly 30 percent at saturation. This
effective area factor included some indeterminate dynamic effects. It was found that variations in cube strength with pore water content could be expressed as a linear function of the product of hydrostatic stress according to the Kelvin equation and the apparent effective area. Attempts to remove the discontinuity in shrinkage strain vs hydrostatic stress curves using effective area factors obtained in the swelling pressure test were, however, not successful.

*THIS PAPER is concerned with physical interaction between evaporable water in cement paste and the solid host to which it is attached. In the context of the Powers (1, 2) models of partially saturated paste, the stresses in pore water are seen as part of an equilibrium system involving the following forces:

1. Cohesive forces between the primary solid particles of which the gel is composed, such forces being visualized as bridging spaces of molecular dimensions;
2. Film or swelling pressure in that part of the pore water which is adsorbed in the gel; force due to this pressure is equilibrated partly by cohesive forces between the enclosing solid surfaces and partly by hydrostatic tension in condensed water;
3. Compression of elementary particles of the solid by surface tension of the solid as modified by changes in surface energy due to sorbed water;
4. Hydrostatic tension in condensed capillary water which is equilibrated partly by elastic compression of the porous structure and partly by a component of the swelling pressure;
5. Vapor pressure in space bounded by the menisci of condensed capillary water; and
6. External mechanical load which superimposes tensile or compressive stresses on the internal stress system of the solid.

The readily observable effects of change in moisture content on strength (3), dimension changes (1, 2, 4, 5, 6) and creep (7, 8, 9, 10) of concretes, mortars and cement pastes can be explained in terms of the model described above.

The model imposes a clearly defined classification of evaporable water: (a) water which is adsorbed onto the surface of elementary particles in the gel is that which is held at low vapor pressures; and (b) condensed capillary water is that which is held at high vapor pressures.

The condition governing the existence of capillary water is related to the fracture strength of water which reaches its limiting value at relative vapor pressures of between 0.40 and 0.45 (2). This coincides with Power's observations (1, 2) that adsorbed gel water is that which is held at vapor pressures below about 0.40 and further, that such water is not subject to capillary condensation.

Feldman and Sereda (11) on the other hand concluded that menisci could exist at vapor pressures as low as 0.31. Whatever value is accepted it is clear that the mechanism of interaction between pore water and solid is different above and below the critical vapor pressure at which menisci can exist.

**Dimension Changes as a Function of Hydrostatic Stress in Pore Water**

In describing the effect of drying from an initially saturated state, Powers (2) has postulated that where menisci exist, the surface tension forces are operative over the whole area of the solid. Thus, neglecting the effect of swelling pressure, the relation between shrinkage strain and equilibrium vapor pressure might be expressed in the form of a simple stress-strain relationship involving hydrostatic tension as determined by the Kelvin equation and the elastic modulus of the porous solid.

Shrinkage strains at equilibrium vapor pressures below this critical value may be ascribed to reduction of swelling pressure in gel water. This pressure may be taken as approximately equal to the potential swelling pressure in a rigid gel (1).

The state of stress in pore water may, therefore, be described as a continuous function of relative humidity throughout the entire range of moisture contents from
saturation to the bare surface condition and its value calculated from the Kelvin equa-
tion. Estimation of the equilibrating stresses in the solid depends upon the adoption of
a reduction factor for the "effective area" of the solid which is in contact with gel
water. Translation of the change of stress in the solid into corresponding dimensional
change also requires a knowledge of the elastic modulus of the solid.

The above treatment of sorption-length-change phenomena neglects the effect of
elastic forces in the solid (insofar as these forces affect both the potential swelling
pressure and the dimensions of primary particles).

A mathematical description of this model of sorption-length-change phenomena may
be set forth as follows (symbols used are defined in the Appendix of this report): for
0.45 < p/p_s < 1, the linear shrinkage strain ε_s1 is given by

\[ \varepsilon_{s1} = \frac{1}{E'} \frac{RT}{MV} \log_e \left( \frac{p}{p_s} \right) \] (1)

and for 0 < p/p_s < 0.45, the linear shrinkage strain ε_s2 is given by

\[ \varepsilon_{s2} = \frac{A_e}{A_g} \frac{1}{E'} \frac{RT}{MV} \log_e \left( \frac{p}{p_s} \right) \] (2)

where E', the effective elastic modulus of the solid, is a function of the time-dependent
deformation characteristics of the cement paste. Though V varies with p/p_s and is less
than the specific volume of liquid water for Eq. 1 and greater than this value for Eq. 2,
it is often assumed to be constant. The effective area, A_e/A_g, presumably varies
with the extent to which the solid surface is covered by water molecules.

E' can be likened to the secant modulus obtained in a creep experiment and is the
ratio of applied stress to the total strain (elastic + plastic + time-dependent or deferred
strain). Although indeterminate, its value should be somewhere near that of the porous
solid.

Dimension Change and Variation of Surface Energy

An alternative approach to the mathematical description of sorption-length-change
phenomena invokes the concept of solid surface tension. This operates on the surface
of elementary particles as a two-dimensional stress system which is equilibrated by
elastic stresses in the solid. Sorption of gas or vapor onto the surface changes the
solid surface tension so that volume changes occur by elastic recovery of the solid on
adsorption and elastic compression on desorption. In this context change in surface
tension may be approximated to change in free surface energy. It may be noted that
the thermodynamically stable state of minimum surface energy would require that the
elementary particles of a porous body should coagulate into a sphere of zero porosity
(12, 13, 14, 15).

Bangham and his associates (12, 16, 17, 18) observed that length changes in charcoal
and coal resulting from adsorption of several different gases and vapors could be ex-
pressed as an approximately linear function of corresponding changes in free surface
energy,

\[ \varepsilon_s = \frac{\Sigma \rho}{E} \Delta F \] (3)

It was clear that the interplay of surface forces and internal pressures was depen-
dent on the geometry of primary particles and that the elastic modulus E was not nec-
essarily that of the gross structure.

Yates (13) considered a model in which the primary particles comprising the porous
solid were spheres in hexagonal close packing joined by welds at their points of con-
tact. Having thus simplified the geometrical aspects of the equilibrium of elementary
particles, he developed the following expression:
\[ K = \frac{4}{9} \sum \rho \frac{d\pi}{d\epsilon_s} \quad (4) \]

where

\[ \pi = \frac{RT}{\Sigma \epsilon_s} \int_{0}^{p} \frac{\nu}{p} dp \quad (5) \]

is the Harkins and Jura (19) expression for \( \pi \), the change in surface energy.

Re-writing Eq. 4 in terms of swelling strain, \( \epsilon_{s3} \), and the elastic modulus \( E \), gave an equation similar to Eq. 3,

\[ \frac{d\epsilon_{s3}}{d\pi} = \frac{\Sigma \rho}{E} \quad (6) \]

Yates' experiments generally confirmed the linear character of Eq. 6 for the sorption of a wide range of nonpolar gases onto porous glass. Some deviation from linearity was noted in regions of very low pressure, where the rate \( d\epsilon_{s3}/d\pi \) was greater than in the linear portion of the curves. Analysis of Yates' results gave estimates for \( E \) of about \( 10.5 \times 10^8 \) psi. Values of \( E \) in this range are considered reasonable for primary particles of glass but not for the porous structure as a whole.

Although the analogous Hooke's Law relationship of Eq. 6 was more or less confirmed by other investigators (20), Feldman and Sereda (14, 15), working on compacts of cement paste, observed several complicating factors:

1. In the low pressure region the relationship in Eq. 6 is affected by the different behavior of interlayer and adsorbed water; the linear character of the equation is, therefore, dependent on the location of a datum point which marks the start of adsorption and which should be chosen so as to exclude the effects of dehydration;
2. At pressures as low as \( p/p_S = 0.31 \) the existence of menisci may superimpose upon Eq. 6 a separate stress system similar to that of Eq. 1; and
3. The general validity of Eq. 6 is inconsistent with observed hysteresis on the drying and wetting cycles and with apparently irreversible components of shrinkage and moisture loss.

Anomalous linear expansions on desorption, such as discussed by Flood and Heyding (21) and Flood and Huber (22), were not observed in hydrated cement. Referring to the work of Feldman and Sereda (14, 15), it would seem that, with respect to hardened cement pastes, both sides of Eq. 6 should also be subject to factors such as (a) variation of cohesive forces between primary particles, and (b) the geometrical requirements of sorbed water (1, 12).

Scope of the Experiments

Equations 1 to 6 represent highly simplified models of the mechanism of shrinkage and swelling in hardened cement paste. True appreciation of the extent to which approximations involved in the basic assumptions and ignorance of other influential factors affect the proposed models requires extensive experimentation. The tests which form the subject of this paper are only part of a more comprehensive investigation. Those parts selected for presentation fall into the following categories:

1. Linear shrinkage and swelling was observed for cement paste and mortar specimens which were allowed to reach equilibrium in atmospheres of various relative humidities;
2. The variation of cube strength was observed for concrete specimens brought to equilibrium in atmospheres of varying relative humidity; and
3. Direct measurements of swelling pressure were obtained on specimens exposed to various ambient relative humidities and longitudinal dimensional restraint.
### TABLE 1
SHRINKAGE AND SWELLING TESTS—PROPERTIES OF MATERIALS USED

<table>
<thead>
<tr>
<th>Cementitious Material</th>
<th>Chemical Composition (%)</th>
<th>Specific Surface (cm²/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Portland cement</td>
<td>22.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Blast-furnace slag</td>
<td>32.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Milled quartzite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2
SHRINKAGE AND SWELLING TESTS—WEIGHT PROPORTIONS AND NONEVAPORABLE WATER

<table>
<thead>
<tr>
<th>Mix</th>
<th>Portland Cement</th>
<th>Blast-Furnace Slag</th>
<th>Quartzite</th>
<th>w₀</th>
<th>wₙ at 7 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC.25</td>
<td>1</td>
<td>—</td>
<td>—</td>
<td>0.25</td>
<td>.120</td>
</tr>
<tr>
<td>PC.50</td>
<td>1</td>
<td>—</td>
<td>1.00</td>
<td>0.50</td>
<td>.149</td>
</tr>
<tr>
<td>PC.80</td>
<td>1</td>
<td>—</td>
<td>2.20</td>
<td>0.80</td>
<td>.159</td>
</tr>
<tr>
<td>PS.25</td>
<td>0.5</td>
<td>0.5</td>
<td>—</td>
<td>0.25</td>
<td>.084</td>
</tr>
<tr>
<td>PS.50</td>
<td>0.5</td>
<td>0.5</td>
<td>1.00</td>
<td>0.50</td>
<td>.121</td>
</tr>
<tr>
<td>PS.80</td>
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<td>0.5</td>
<td>2.20</td>
<td>0.80</td>
<td>.136</td>
</tr>
</tbody>
</table>

### TABLE 3
SALT SOLUTIONS USED TO CONTROL RELATIVE HUMIDITY

<table>
<thead>
<tr>
<th>Saturated Salt Solution</th>
<th>NaOH</th>
<th>LiCl</th>
<th>CaCl₂</th>
<th>K₂CO₃</th>
<th>Ca(NO₃)₂</th>
<th>NaCl</th>
<th>KCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative humidity, p/p₀</td>
<td>0.070</td>
<td>0.150</td>
<td>0.320</td>
<td>0.440</td>
<td>0.560</td>
<td>0.765</td>
<td>0.864</td>
</tr>
</tbody>
</table>

### TABLE 4
SWELLING PRESSURE TEST—PROPERTIES OF PORTLAND CEMENT USED

<table>
<thead>
<tr>
<th>Chemical Composition (%)</th>
<th>Specific Surface (cm²/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>22.4</td>
<td>2.2</td>
</tr>
</tbody>
</table>

### TABLE 5
SWELLING PRESSURE TEST—WEIGHT PROPORTIONS AND NONEVAPORABLE WATER AT START OF DRYING

<table>
<thead>
<tr>
<th>Portland Cement</th>
<th>Milled Quartzite</th>
<th>Crusher Sand</th>
<th>w₀</th>
<th>wₙ</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7</td>
<td>1.3</td>
<td>0.60</td>
<td>0.152</td>
</tr>
</tbody>
</table>
EXPERIMENTAL

Shrinkage and Swelling Tests

It was decided to conduct the tests on pastes having three water/cement ratios and to investigate the effect of replacing half of the weight of cement with blast-furnace slag. In order to minimize as far as possible the effects of bleeding, siliceous sand milled to cement fineness was added to produce stiff mixes which were, for practical purposes, non-bleeding. The main characteristics of the materials are given in Table 1 and the mix proportions are given in Table 2.

The specimens were prisms measuring 3/4 in. by 3/4 in. by 6 in. In choosing this size a compromise was sought between the period taken to reach equilibrium with the ambient atmosphere and the capacity of the specimens to remain sensibly constant in weight and length during the short period of exposure to the laboratory atmosphere while readings were being taken. The specimens were cast in the direction of their length so that possible variations in water/cement ratio were averaged out over the gage length of 4 in. For each of the six mixes 16 prisms were prepared for test at each of three ages. Half of the prisms of each mix were oven-dried at 110 C for two days prior to test and the remainder were placed in the appropriate environment in an initially saturated condition.

The prepared specimens were placed on an expanded metal rack in a steel drum which contained a shallow glass dish holding a supersaturated salt solution. The lid of the drum was fitted with a rubber gasket and two good quality stopcocks. Once the specimens had been sealed into the drum one stopcock was connected to a manifold which in turn was connected to one or two rotary vacuum pumps. When the vacuum pumps were started the specimens were subjected to a drying action limited by the vapor pressure over the salt solutions. The whole assembly was kept in a cabinet in which the temperature was controlled at 25 ± 1 C.

Change in length was measured by means of a Demec (23) strain gage used with the specimen supported on a rubber mat. Water loss was obtained by weighing on a micro-balance. The end point of drying in a particular ambient atmosphere was arbitrarily defined as the stage at which measurable change in length was less than 0.002 percent per week.

The salt solutions used and the assumed value of the respective relative humidites are given in Table 3.

Swelling Pressure Test

The main characteristics of the materials and mixes used in the swelling pressure test are given in Tables 4 and 5. The specimens consisted of prisms 3 in. square in cross-section and 18 in. long, cast with a centrally placed longitudinal hold, 3/8 in. in diameter.

For the present tests two prisms were cast and cured in water for seven days before being exposed to vacuum drying in a steel drum in which the space around the specimens was kept filled with freshly activated silica gel. In the later stages of drying the specimens were removed from the drum and heated to 60 C in an oven and then, while still warm, subjected to vacuum drying.

After some 15 months the prisms had lost about 98 percent of the weight lost by a companion control specimen which had been oven-dried at 110 C for 7 days. The linear shrinkage of the slowly dried specimens was more than double that of the control specimen.

One prism was placed in the apparatus shown in Figure 1. In this apparatus load was applied to the specimen by means of a 7-mm diameter high tensile steel wire which was passed through it and anchored to the lower steel loading plate. The upper steel loading plate reacted against the plunger of a mechanical jack. The steel wire passed through a hole drilled on the axis of the plunger and was attached to a yoke suspended from a knife-edge bearing on one end of the loading beam. Dead weight could be applied to the other end of the beam in order to place the specimen in compression. The wire was fitted with a sensitive extensometer which could be used...
as an interpolation device, thus enabling the stress in the specimen to be regulated with a sensitivity of 1 psi. The total available range was 0-1200 psi.

Shrinkage and swelling strains were measured over the whole length of the specimen by means of a pair of dial micrometers having a strain sensitivity of $5.56 \times 10^{-4}$ percent per division.

The circular steel bearing plates were equipped with rubber o-rings so that a transparent plastic cylinder could be forced over the ends, thus creating an enclosed vessel containing the prism. Suitable inlets were provided in order to allow air, conditioned to the required relative humidity by means of acid or salt solutions in a train of gas washing bottles, to be passed through the cell in a continuous stream. The second specimen was enclosed in a similar cell connected to the same air stream but subject only to light mechanical loading.
The loaded specimen was at first subjected to an axial stress of 1200 psi while an air stream conditioned in concentrated sulfuric acid was passed through the cell. When all creep had ceased, the axial stress was reduced to 600-psi and air, conditioned to a low relative humidity, was admitted to the cell. The load was then progressively adjusted so as to keep the length constant at the 600-psi dry state value. At the same time, the unrestrained change in length of the companion specimen was observed. After equilibrium at a particular relative humidity had been attained, the air stream was conditioned to the next higher humidity value and the process repeated.

**Strength Tests**

Selected properties of the basic materials and the mix proportions of the mortars used are recorded in Tables 6 and 7.

Twenty-eight 2-in. cubes were cast from each mix and cured in water for 14 days. The cubes of each mix were divided into seven batches of four, one batch being crushed immediately while in a saturated condition, and a second batch being similarly tested after drying at 110 C for one week.

The remaining five batches in each mix were dried to different moisture contents by simultaneous warming and vacuum drying at about 60 C. This process took about one week to complete. At the end of the drying period, the five batches from each mix were divided and placed in five steel drums, each of which was fitted with a calibrated hygrometer and the usual arrangement for evacuation. Each drum, containing 12 cubes, 4 from each mix, was evacuated and then sealed. When the specimens appeared to have reached equilibrium with each other and the surrounding atmosphere, which usually took about one week, they were removed from the drum and tested. The reading on the hygrometer was taken as the equilibrium relative humidity and the corresponding moisture content was determined by weighing.

**RESULTS**

**Shrinkage and Swelling Tests**

The results of shrinkage and swelling tests are summarized in Table 8, the observed quantities $w_o$ and $e_s$ being referred to the final oven-dried state in each case. This
## Table 8: Results of Shrinkage and Swelling Tests

<table>
<thead>
<tr>
<th>Mix</th>
<th>Cycle&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Obs. Qty.</th>
<th>Oven Dried</th>
<th>p/p&lt;sub&gt;5&lt;/sub&gt;</th>
<th>0.070</th>
<th>0.150</th>
<th>0.320</th>
<th>0.440</th>
<th>0.560</th>
<th>0.765</th>
<th>0.864</th>
<th>1.000</th>
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<tbody>
<tr>
<td>PC. 25</td>
<td>NTD</td>
<td>w&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.045</td>
<td>0.250</td>
<td>0.200</td>
<td>0.141</td>
<td>0.115</td>
<td>0.085</td>
<td>0.067</td>
<td>0.067</td>
<td>0.102</td>
<td>0.119</td>
</tr>
<tr>
<td></td>
<td>NTA</td>
<td>w&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.045</td>
<td>0.240</td>
<td>0.233</td>
<td>0.200</td>
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<td>0.187</td>
<td>0.172</td>
<td>0.172</td>
<td>0.156</td>
<td>0.166</td>
</tr>
<tr>
<td></td>
<td>ODA</td>
<td>w&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.350</td>
<td>0.297</td>
<td>0.286</td>
<td>0.239</td>
<td>0.206</td>
<td>0.185</td>
<td>0.168</td>
<td>0.172</td>
<td>0.185</td>
<td>0.198</td>
</tr>
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<td>NTD</td>
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<td>0.0472</td>
<td>0.0551</td>
<td>0.0791</td>
<td>0.0988</td>
<td>0.1118</td>
<td>0.1275</td>
<td>0.1403</td>
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<td></td>
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<td>0.151</td>
<td>0.140</td>
<td>0.133</td>
<td>0.125</td>
<td>0.117</td>
<td>0.117</td>
<td>0.098</td>
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<tr>
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<td>0.284</td>
<td>0.190</td>
<td>0.189</td>
<td>0.185</td>
<td>0.172</td>
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<td>0.144</td>
<td>0.128</td>
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<td>PC. 80</td>
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<td>0.150</td>
<td>0.134</td>
<td>0.133</td>
<td>0.125</td>
<td>0.117</td>
<td>0.117</td>
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<td>0.173</td>
<td>0.167</td>
<td>0.159</td>
<td>0.149</td>
<td>0.145</td>
<td>0.145</td>
<td>0.126</td>
<td>0.084</td>
</tr>
<tr>
<td>PS. 25</td>
<td>NTD</td>
<td>w&lt;sub&gt;0&lt;/sub&gt;</td>
<td>0.469</td>
<td>0.566</td>
<td>0.251</td>
<td>0.227</td>
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<td>0.469</td>
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<td>0.153</td>
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<td>0.256</td>
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<td>0.437</td>
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<td>0.302</td>
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<td>0.192</td>
<td>0.192</td>
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<tr>
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<td>0.0210</td>
<td>0.0304</td>
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<td>0.0813</td>
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<td>0.2611</td>
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<td>0.339</td>
<td>0.339</td>
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</tbody>
</table>

<sup>a</sup>NTD = Desorbing from saturation at 25 C; NTA = Adsorbing after drying cycle NTD at 25 C; ODA = Adsorbing after oven-drying for 4 days at 110C.

The observed variations of shrinkage or swelling with moisture content are presented in Figures 2, 3 and 4. The results of only four samples were plotted for the following reasons: (a) some specimens were accidentally broken in certain of the original groups of 8 but there were always at least 5 specimens which completed the whole cycle; and (b) except perhaps for the confused area in the region of the monolayer capacity, the curves were coincident within the limits of experimental accuracy. In the interests of clarity and uniformity, therefore, only results of the first four surviving specimens were plotted.

## Calculations Used in Reducing Results of Shrinkage and Swelling Tests

The Kelvin equation representing the hydrostatic tension part of Eq. 1 was evaluated in the form

$$\Delta P = \frac{RT}{MV} \log e \left( \frac{p/p_s}{5} \right)$$

$$= 3120 \log_{10} \left( \frac{p/p_s}{5} \right) \text{ atmospheres} \quad (7)$$
Figure 2. Shrinkage vs moisture loss for desorption cycle: (a) portland cement; (b) 50/50 portland cement/blast-furnace slag.
Figure 3. Shrinkage vs moisture loss for adsorption cycle on specimens dried at 25°C: (a) portland cement; (b) 50/50 portland cement/blast-furnace slag.
Figure 4. Shrinkage vs moisture loss for adsorption cycle on oven-dried specimens: (a) portland cement; (b) 50/50 portland cement/blast-furnace slag.
In Eq. 7 it was assumed, contrary to fact, that $V = 1$ for all values of hydrostatic tension and pressure.

Plots of $\Delta P$ vs $\varepsilon_S$ are presented in Figures 5, 6 and 7.

The monolayer capacities, $V_m$, were calculated from a least-squares fit of the BET equation. These are given in Table 9 and are also shown in Figures 2, 3 and 4.

Harkins and Jura (19) and Yates (13) evaluated Eq. 5 by a graphical method. In the present series the same process was carried out algebraically.

It was first necessary to fit the experimental data to an equation of the form

$$\frac{V}{p} = A_0 + A_1 p + A_2 p^2 + \ldots + A_n p^{n+1} \tag{8}$$

The coefficients $A_0, A_1, \ldots$ converged rapidly to zero but it was found necessary to use 8 significant figures. For example the data of mix PC 25 NTD yielded the equation

$$\frac{V}{p} = 0.02988503 + 0.00671467 p + 0.00071773 p^2 + 0.00002588 p^3$$

$$+ 0.00000073 p^4 + 0.00000007 p^5$$

with a standard deviation of 0.0003 in the value of $V/p$.

The equations for each group of specimens were integrated in steps of 2-mm pressure over the range $p = 0$ to $p = 23.76$ mm Hg, using Eq. 5 in the form

$$\pi = \frac{1.3753 \times 10^6}{\Sigma \text{BET}} \int_0^p \frac{V}{p} dp \text{ ergs/cm}^2 \tag{9}$$

where $\Sigma \text{BET}$ was the surface area obtained from the monolayer capacity and the assumption that the area covered by a water molecule is $10.6 \text{ Å}^2$, and $V$ was measured in grams of water per gram of cement. Plots of $\pi$ vs $\varepsilon_S$ are presented in Figures 8, 9 and 10.

Swelling Pressure Tests

Observations of $\sigma_g$, the externally applied axial stress needed to maintain constant length of an initially dry specimen, are plotted against $p/p_g$ in Figure 11.

On the assumption that swelling pressure is effective over a portion $A_e$ of the gross cross-sectional area $A_g$, the following equation relates the externally applied mechanical stress to changes in the hydrostatic stress in pore water:

$$\sigma_g = \frac{A_e}{A_g} \Delta P \tag{10}$$

in psi. Values of $A_e/A_g$ computed from this equation are shown in Figure 12.

It should be noted that the value of $\sigma_g$ for $p/p_g = 1$ was calculated from the free length change of the swelling pressure specimen. This was considered justified by the constancy of the elastic modulus found in loading the specimen at various values of $p/p_g$. The points shown in Figure 12, therefore, include interpolated values of $A_e/A_g$ up to $p/p_g = 0.5$ and extrapolated values between $p/p_g = 0.5$ and $p/p_g = 1.0$. 
Figure 5. Shrinkage as a function of $\Delta P = 3120 \log_{10} (p/p_s)$ for desorption cycle: (a) portland cement; (b) 50/50 portland cement/blast-furnace slag. Note: $\Delta P$ for maximum shrinkage is indeterminate.
Figure 6. Shrinkage as a function of $\Delta P = 3120 \log_{10} (p/p_5)$ for adsorption on specimens dried at 25°C: (a) portland cement; (b) 50/50 portland cement/blast-furnace slag.
Figure 7. Shrinkage as a function of $\Delta P = 3120 \log_{10} \left( \frac{p}{p_s} \right)$ for adsorption on oven-dried specimens: (a) portland cement; (b) 50/50 portland cement/blast-furnace slag.
Figure 8. Shrinkage as a function of Eq. 9 for desorption cycle: (a) portland cement; (b) 50/50 portland cement/blast-furnace slag.
Figure 9. Shrinkage as a function of Eq. 9 for adsorption on specimens previously dried at 25°C: (a) portland cement; (b) 50/50 portland cement/blast-furnace slag.
Figure 10. Shrinkage as a function of Eq. 9 for adsorption on oven-dried specimens: (a) portland cement; (b) 50/50 portland cement/blast-furnace slag.
TABLE 9
MONOLAYER CAPACITY AS DETERMINED BY THE BET EQUATION

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<tr>
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<th>Cycle</th>
<th>( V_m )</th>
<th>Mix</th>
<th>Cycle</th>
<th>( V_m )</th>
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<tr>
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<td>PS.25</td>
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<td>NTD</td>
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TABLE 10
STRENGTH OF MORTAR CUBES

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<tr>
<th>Mix</th>
<th>Oven-Dried</th>
<th>( p_{/p_s} ) (psi)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>0.12</td>
<td>0.24</td>
</tr>
<tr>
<td>PC.65</td>
<td>9660</td>
<td>8500</td>
</tr>
<tr>
<td>PS.65</td>
<td>10200</td>
<td>9150</td>
</tr>
<tr>
<td>PC.75</td>
<td>8880</td>
<td>7960</td>
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</table>

Figure 11. Relationship between observed swelling pressure on gross cross section and relative humidity.
Figure 12. Relationship between relative humidity and proportion of gross cross-sectional area acted upon by pore water pressure.

Figure 13. Relationship between change in cube strength and product of $\Delta P = 3120 \log_{10} \left( \frac{p}{p_0} \right)$ and effective area.
**Strength Test**

Cube crushing strengths of specimens brought to equilibrium at various values of \( P/P_S \) are given in Table 10. The mean apparent increase in cube strength consequent upon drying is shown plotted against \((A_e/A_g)/\Delta P\) in Figure 13.

**DISCUSSION**

This study is restricted to an investigation of the Powers (1, 2) model of hardened cement paste and the extent to which the behavior of such a model conforms with the analogous stress-strain relationship (Eqs. 1, 2 and 6).

**Shrinkage and Swelling**

It is seen (Figs. 2, 3 and 4) that curves of shrinkage strain vs moisture loss show discontinuities at different values of the ratio of evaporable water to monolayer capacity according to whether the sample is adsorbing or desorbing. Curves representing the desorption cycle are similar to those published by Alexander and Wardlaw (6) with the characteristic discontinuity occurring at about one monolayer capacity and with a clearly defined double inflection. On adsorption the discontinuity appears between 2 and 4 monolayers capacity and the existence of a double inflection is less well defined.

The first point of inflection before the discontinuity, on the desorption cycle, might possibly be ascribed to the Pickett (4) effect. Surface cracking is thought to be present in some degree on all drying specimens as the electron micrographs of Figure 14 suggest. Figure 14a depicts the appearance of a highly polished surface of PC.25 cement paste at the start of the NTD cycle. Figure 14b shows the appearance of the specimen when \( r_S \) was about 0.03 percent. Explanation of the deceleration of the shrinkage rate is based on the concept of differential stresses existing across any cross section of the specimen due to moisture gradients. Before cracking, the outer fibers would be in tension and the inner fibers in compression. Surface cracking would, in these circumstances, disturb the balance of stresses acting on lateral planes and result in slight expansion. This would appear as a reduction in the rate of shrinkage. Such as argument would not, however, explain similar points of inflection on the adsorption cycle.

An alternative explanation, in respect to the drying cycle only, visualizes the film pressure of gel water as balanced partly by tension in capillary water and partly by cohesive forces in the solid. Sudden release of one stress, namely the surface tension, at about the monolayer capacity, might allow "rebound" of the pore water into gel space.

On adsorption from the bare surface condition, the appearance of menisci might be preceded by the formation of clusters of water molecules several layers deep before the establishment of a continuous film. This mechanism of sorption, if true, would result in a deceleration of the rate of swelling with respect to water gain. This hypothesis would also explain the occurrence of the discontinuity at different monolayer capacities on wetting and drying cycles.

The experimental data of Figures 2, 3 and 4 are too scattered to allow confirmation of the degree of nonlinearity observed at low pressures by Feldman and Sereda (14, 15). The existence of a linear relationship between dimension change and gain or loss of moisture in the adsorption region is evidently confirmed by the observations shown in Figures 2, 3 and 4.

The expected discontinuity in the relationship between \( \Delta P \) as calculated by Eq. 7 and shrinkage for the drying cycle is clearly seen in Figures 5, 6 and 7, but does not in all cases occur at the expected value of \( \Delta P = 1100 \) atmospheres. Table 11 gives a comparison of the effective elastic modulus \( E' \) calculated from Eq. 1 and values obtained experimentally in a static loading test. These results appear to be anomalous since the value of \( E' \) increases with the initial water/cement ratio \( w_0 \) in the case of portland cement mixes and exhibits the opposite trend in mixes containing blast-furnace slag. In this connection, if cracking of the outer fibers and decompression of the core caused an apparent reduction in shrinkage, \( E' \) would have a relatively high value, but the
Figure 14. (a) Polished surface of specimen PC.25 before drying; (b) same specimen after shrinkage $\epsilon_s = 0.03$ percent had taken place (side of each photograph = approximately $5\mu$).
TABLE 11
ELASTIC MODULUS $E_s$ COMPARED WITH $E'$ CALCULATED FROM EQUATION 1

<table>
<thead>
<tr>
<th>Mix</th>
<th>Elastic Modulus $(10^6 \text{ psi})$</th>
<th>Mix</th>
<th>Elastic Modulus $(10^6 \text{ psi})$</th>
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<tbody>
<tr>
<td></td>
<td>$E_s$</td>
<td></td>
<td>$E'$</td>
</tr>
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<td>PC.25</td>
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<td>PS.25</td>
<td>3.45</td>
</tr>
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<td>PC.50</td>
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<td>PS.50</td>
<td>2.62</td>
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<tr>
<td>PC.80</td>
<td>2.31</td>
<td>PS.80</td>
<td>1.95</td>
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</tbody>
</table>

overall shrinkage would be relatively low. The opposite trend is observed in both PC and PS specimens and thus the effect shown in Table 11 must, for the time being, be ascribed to experimental vagaries.

As might be expected, the Powers model is not followed as closely on the desorption cycles as on the adsorption cycles, but it is nevertheless clear that discontinuities are associated with the disappearance of menisci. The appreciable nonrecoverable shrinkage strains might arise from plastic flow at point-to-point contacts of primary particles and closure of spaces which originally accommodated adsorbed water in "areas of obstructed adsorption" (2).

It might be expected that if the correct value of $A_e$ had been known and the quantity $(A_e/A_g)/\Delta P$ plotted against $\epsilon_s$, the desorption curve would be nearly linear throughout. Application of values of $A_e/A_g$ from Figure 12 to the results shown on Figures 5, 6 and 7 failed, however, to eliminate the discontinuity. For the sake of brevity this part of the work is omitted.

Plots of $\pi$ vs $\epsilon_s$ in Figures 8, 9 and 10 show that both the adsorption and desorption cycles yield sigmoidal curves. The curves relating to adsorption from the oven-dry condition (Fig. 10) are, however, nearly linear with values of $E$ which are close to those obtained by Yates (13) for the adsorption of argon on porous glass. On both adsorption and desorption for specimens kept at 25°C, the first inflection of the sigmoidal curve in most cases occurs at about $p/p_s = 0.45$ and the second at about $p/p_s = 0.07$. This seems to be in agreement with the observations of Feldman and Sereda (14, 15) regarding the effects of interlayer water in the low-pressure region and condensation in the high-pressure region.

Regarding the near-linearity of $\pi$ - $\epsilon_s$ curves in the case of initially oven-dried specimens (Fig. 10), it is thought that the effect of heat treatment may have converted some of the colloidal products of hydration to crystalline material of lower surface area. Under such circumstances the secondary effects of film pressure in areas of restricted adsorption (2) would be diminished. The effects of meniscus formation in the region of $p/p_s = 0.45$ do, however, appear in some of the curves shown in Figure 10 and, as in the case of Yates' experiments, appear to be of secondary importance.

These tests suggest that profound changes of structure occur on the desorbing cycle. The sequential photographs of Figure 15 depict the collapse of gel structure which is often observed in the electron microscope. It seems likely that a similar phenomenon occurs when cement paste is dried for the first time. The work of Tomes, Hunt and Blaine (24) demonstrated a progressive reduction of surface area on successive cycles of adsorption and desorption. A similar effect is seen in the values of $V_m$ given in Table 9. This could be accounted for by progressive closure of gaps between primary particles in the gel which were originally only a few Angstrom units wide.

Considering deviations from linearity of the $\pi$ - $\epsilon_s$ curves of Figures 8, 9 and 10 in relation to the force system described at the beginning of this paper, it is clear that the third effect cannot be divorced from the first, second and fourth effects nor from progressive changes in the structure of hardened cement paste.
Figure 15. Sequence showing collapse of gel structure of specimen dehydrating in electron microscope (side of each photograph = approximately 10 μ).
Strength Tests

Mills (3) reported that cube strength appeared to vary systematically with moisture content but was not greatly affected by saturation in large molecular fluids such as kerosene. From this he postulated that, since water was capable of occupying sites in the gel structure which were not available to the larger molecules (1, 3), film pressure in areas of restricted adsorption resulted in loss of strength due to weakening of cohesive solid surface to solid surface bonds.

The results of Figure 13 support the view that the effects of external load are modified by the internal stress system. Relaxation of internal stress results in an increase of uniaxial crushing strength in a manner analogous to that experienced in a triaxial strength test. The state of stress in pore water is a measure of the variation of triaxial tension in the skeletal structure of the solid.

TENTATIVE CONCLUSIONS

1. The results of the experimental work are in general agreement with the Powers model of the structure of cement paste and the concept of the equilibrium of forces between solid and pore water. The existence of swelling or film pressures in areas of restricted adsorption is in keeping with the observed variations of strength and effective swelling pressure at low values of p/p_s. The theoretical values of swelling pressure, however, depend on inadmissible assumptions and calculation of the effect of such pressures involves the estimation of "effective area" which remains indeterminate.

2. Strains in elementary particles of hydrated cement resulting from variation of surface energy constitute a significant contribution to the overall dimension changes. The stress system associated with these strains is unlikely to have any significant effect on strength but cannot be ignored in respect to volume change.

3. The volume changes accompanying gain or loss of moisture in hardened cement paste are not, at the present stage, amenable to mathematical treatment as a simple Hooke's Law phenomenon. Three main stress systems visualized as contributing to the overall volume changes are (a) the reaction of menisci forces on the porous solid, (b) the reaction of swelling or film pressure on the porous solid, and (c) the reaction of solid surface tensions on elementary particles of the porous solid. The stress systems (a) and (b) may be described in terms of the Kelvin and Gibbs equations, respectively and each predominates in a separate zone of the isotherm. Both equations depend on assumptions which are not strictly correct. Expression of the stress system (b) in terms of the potential swelling pressure ignores the modifying influence of elastic strains in the porous solid and is also based on other incorrect assumptions. Successful adaptation of these stress systems is further limited by lack of knowledge of the effective areas of interaction and of the elastic constants of both the porous solid and of the elementary particles of which it is comprised.

4. Mathematical description of the behavior of hardened paste is further handicapped by the ever-changing nature of the porous solid. Even in the fully hydrated compacts of Feldman and Sereda the complicating effects of dehydration, sintering and reduction of surface area were evident. Under normal circumstances the stress systems would be modified by particles of unhydrated cement and aggregates, while other basic parameters would be subject to continual change due to hydration of the cement.

ACKNOWLEDGMENTS

The author's thanks are owed to C. W. Wolhuter and H. I. Schwartz, who read the first draft of this paper and made helpful suggestions, and to Peter Thompson who made many of the observations.

REFERENCES

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Appendix
NOTATION

\[ p = \text{vapor pressure}; \]
\[ p_s = \text{saturation vapor pressure}; \]
\[ p/p_s = \text{relative vapor pressure or relative humidity}; \]
\[ v = \text{volume of adsorbate taken up at pressure } p; \]
\( w_0 \) = initial weight ratio of water/cement;
\( w_n \) = weight ratio of nonevaporable water/cement;
\( w_e \) = weight ratio of evaporable water/cement;
\( A_g \) = cross-sectional area of porous solid;
\( A_e \) = effective area over which film pressure acts at low values of \( p \);
\( E \) = elastic modulus of solid;
\( E' \) = effective elastic modulus of solid;
\( E_S \) = elastic modulus of porous solid obtained by mechanical loading;
\( K \) = bulk modulus of solid;
\( R \) = gas constant;
\( P \) = hydrostatic stress calculated by means of the Kelvin equation;
\( \Delta P \) = change in \( P \);
\( T \) = absolute temperature;
\( M \) = molecular weight of water;
\( V \) = absolute volume of pore water;
\( V_m \) = monolayer capacity as determined by the BET equation;
\( F \) = surface energy of solid;
\( \Delta F \) = change of surface energy in solid;
\( \epsilon_{S1} \) = linear shrinkage in zone where menisci can exist;
\( \epsilon_{S2} \) = linear shrinkage due to evaporation of pore water;
\( \epsilon_{S3} \) = linear shrinkage according to Yates (Eq. 6);
\( \epsilon_S \) = general term denoting shrinkage strain;
\( \rho \) = density of material;
\( \sigma \) = stress usually mechanical;
\( \sigma_g \) = mechanical stress on gross cross section;
\( \pi \) = surface energy of solid;
\( \Sigma \) = surface area of solid; and
\( \Sigma_{BET} \) = surface area of solid calculated by BET method.