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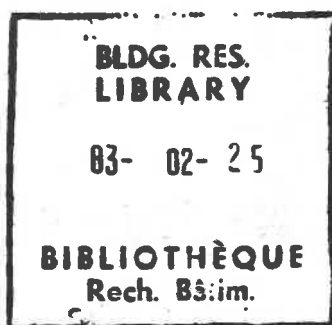
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by G. G. Litvan and R. E. Myers

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## SURFACE AREA OF CEMENT PASTE CONDITIONED AT VARIOUS RELATIVE HUMIDITIES

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### ABSTRACT

The  $N_2$  BET surface area (SA) of bottle hydrated portland cement is greatly reduced if exposed to changing relative humidities. The maximum SA loss, from 83 m<sup>2</sup>/g, occurred on exposure to between 40 and 60% RH. In addition, the number and rate of humidity changes appear to affect the value of the SA, which increases only when exposed to relative humidities in excess of 75%. The phenomenon cannot be explained by the usual causes of aging of high specific SA solids. It is proposed that the solid, deformed by non-uniform moisture distribution during changing humidity conditions, breaks and makes interparticle bonds. A unique feature of cement paste is that these bonds can easily form and remain intact even after the moisture gradient vanishes.

### Introduction

Hunt, Tomes and Blaine (1) reported in 1960 that the BET nitrogen surface area (SA) of hydrated cement paste depends to a great extent on the relative humidity (RH) at which the specimens are stored prior to testing. Generally, there is a decrease in SA, with the greatest loss occurring at an intermediate relative humidity of 40%.

The phenomenon, which has become known as aging, was studied by Collepardi (2), Bye and Chigbo (3), and Parrott, Hansen and Berger (4), but no agreement concerning its cause was reached. Because surface area is one of the most characteristic physical properties of disperse systems, an alteration of its value is indicative of significant changes in the microstructure, with a potential bearing on such important macroscopic phenomena as creep and drying shrinkage. For these reasons an extension of the investigation of SA loss seems useful.

### Method

The SA of the specimens was determined by the volumetric method in a NUMINCO Model MIC 103 apparatus. Prior to measurement a specimen at room temperature was pumped through a liquid nitrogen trap until the residual pressure was less than  $1 \times 10^{-1}$  Pa. In some cases, where so indicated and after determination of SA, specimens were heated to 80 and to 110°C, respectively, during evacuation prior to repeating the measurement to assess the effect of the preparatory treatment on SA.

The level of the liquid nitrogen surrounding the specimen bulb was maintained (automatically) at a constant height ( $\pm 1$  mm).

The SA was calculated from five adsorption points with a correlation coefficient  $>0.9999$ .

Saturated solutions of KBr, NaCl,  $\text{NaNO}_2$ , NaBr,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCl}_2$  and LiCl as well as anhydrous  $\text{Mg}(\text{ClO}_4)_2$  provided constant humidity in glass desiccators in which the specimens were stored. The solutions were stirred with magnetic stirrers for 1 min in every 6-min period in order to minimize heating effects.

### Materials

Type 10 normal portland cement was used that had been bottle hydrated (150 g cement in 750 ml water) in continuous rotation for 288 days. Specimens for storage were obtained by withdrawing a dose of constant volume from the well-mixed suspension with a special pipette. It was centrifuged for 8 min and the clear liquid decanted, yielding a slurry weighing approximately 11 g.

### Procedure

First Series: The sequence of the experimental procedure is shown in Fig. 1.

Point A0: A specimen of the thoroughly mixed, centrifuged slurry was transferred in a gloved box to a vacuum apparatus for drying. The atmosphere in the gloved box was maintained moisture- and  $\text{CO}_2$ -free with anhydrous  $\text{Mg}(\text{ClO}_4)_2$  and Indicarb.

The sample was pumped at room temperature through a liquid  $\text{N}_2$  trap for 28 days, during which time weight loss was less than  $3 \times 10^{-5}$   $\text{gg}^{-1} \text{ day}^{-1}$ . Final degassing to  $1 \times 10^{-1}$  Pa was accomplished by pumping, still at room temperature, in the surface area apparatus. (In some instances, where indicated, the specimen was heated to 80 or 100°C during the last drying step.) The described drying procedure was followed routinely with every specimen investigated in the project. The surface area of the original paste is labelled A0.

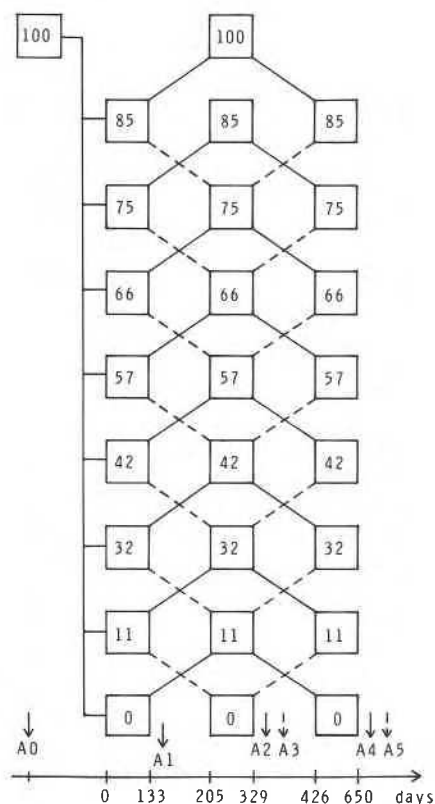


FIG. 1

Sequence of experimental procedures followed in First Series. Numbers in boxes indicate RH

Point A1: At the beginning of the experiment, on 0 day, a thoroughly mixed, centrifuged slurry was placed in each of the eight conditioning desiccators which were then pumped down to 30 KPa pressure. Humidities in the desiccators were 0, 11, 32, 42, 57, 66, 75 and 85%. Conditioning lasted for a minimum of 133 days, during which period the desiccators were left undisturbed in an air-conditioned room. At the end of the storage period 1.5 g samples were removed and prepared for surface area determination.

Points A2 and A3: The remainder of the paste in the eight desiccators was at this stage (205 days after 0 day) divided into two portions; one was transferred to one level higher humidity and the other portion to one level lower humidity. After 124 days of storage the specimens were dried and SA values obtained. The SA values of the specimens conditioned at these humidities were A2 and A3, respectively.

Points A4 and A5: On day 426 the specimens left in the desiccators were returned for 224 days to the humidities at which they had been originally conditioned. A4 and A5 are the SA values of those samples exposed to higher and lower humidities, respectively. Thus A1, A4 and A5 were obtained at the same relative humidity. It should be noted that specimens, once vacuum dried for SA determination, were not replaced in storage unless specifically stated. The entire cycle required 650 days.

Gravimetric Series: Companion specimens to those in the First Series were placed, on 0 day, in a second set of eight desiccators maintained at the same humidity levels as those chosen for the other series. These specimens were weighed periodically to monitor the progress of equilibration of the samples in the First Series. By following this procedure it was not necessary to open the desiccators of the First Series.

The rate of weight change after 28 days of storage was between 70 and  $5 \times 10^{-4} \text{ gg}^{-1} \text{ day}^{-1}$ ; this decreased to between 4 and  $0.7 \times 10^{-4} \text{ gg}^{-1} \text{ day}^{-1}$  at the end of the conditioning period.

Second Series: In a few cases the specimens conditioned at 0, 11, 32 and 42% RH were d-dried ( $7 \times 10^{-2} \text{ Pa}$  water vapor pressure) and following SA determination (A1) were divided into two parts; one portion was re-exposed to 100% RH and the other to the humidity at which the companion A1 was obtained.

Carbonation: The  $\text{CO}_2$  content of the original stock, bottle-hydrated paste, was 0.61%, a value that increased to only 0.96% after it was handled six

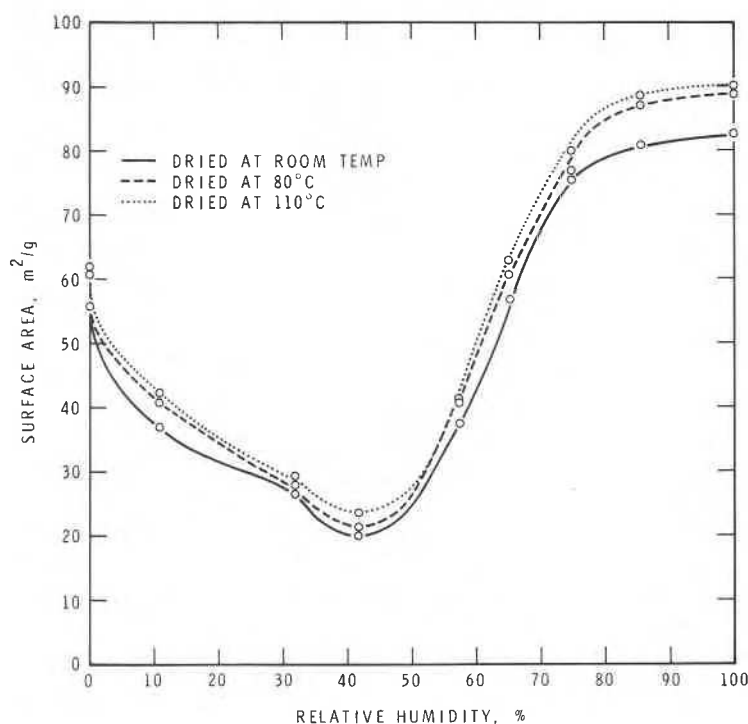


FIG. 2

$N_2$  BET surface area of cement paste stored at various humidities (A1) and dried prior to SA determination of 20, 80 or 110°C

humidities. After conditioning at 42% RH SA was less than 25% of the original value of samples initially conditioned at 100% RH.

These results are in general agreement with those of Hunt et al. (1), although there are significant differences: in the study by Hunt et al. conditioning was not done above 80% RH and the shape of the curve in the 80 to 100% RH region (showing only small changes in SA) was not recorded. Because of the larger number of RH levels in the present study, the curve is generally better defined. At very low humidities Hunt et al. obtained SA values greater than those of the original wet paste, probably the result of high drying rates, the effects of which have been well documented (5). In a recent study Parrott et al. (4) observed low SA values not much larger than those obtained at 40% RH following storage at below 40% RH.

The SA of the A1 points in Fig. 2 for specimens conditioned at various humidities and dried at temperatures of 20, 80 and 110°C prior to SA determination are similar in shape, indicating that the observed features are not affected by the rigidly held water. Elevation of the temperature from 20 to 110°C resulted in 20% higher A1 values. Whether or not chemically bound water was also removed in this process cannot be ascertained. The results once again underline the need for standardizing every aspect of the SA determination if quantitative comparison is contemplated.

times, indicating the effectiveness of the precautions taken to avoid carbonation.

### Results

#### Point A0

The SA value of the original paste on 0 day was  $83.0 \text{ m}^2 \text{ g}^{-1}$ . In the course of the study the determination was repeated several times. The good reproducibility indicated that no further change (such as hydration) affecting SA took place on storing the paste in water.

#### Point A1

The SA values of specimens conditioned at various humidities are shown in Fig. 2. Drastic decrease in SA is particularly noticeable at intermediate

### Points A2 to A5

The SA values of the specimens at the previous stages of the conditioning cycle, A2 to A5, are shown in Figs. 3 and 4. The following observations were made:

- 1) As A2 and A3 are in every case less than the respective A1 values, it is clear that SA loss occurred with changes in humidity to either higher or lower levels.
- 2) For samples originally conditioned at 32, 42, 75 and 85% RH,  $A2 = A3$ ; for those conditioned at 57 and 66% RH,  $A2 > A3$ ; and for those conditioned at 11% RH,  $A2 < A3$ .
- 3) In the range from 11 to 66% RH completion of the humidity cycle by re-establishing the RH of point A1 resulted in a further decrease in SA:  $A2 > A4$  and  $A3 > A5$ .
- 4) At 11% RH  $A4 < A5$ ; between 32 and 57% RH  $A4 = A5$ ; and at 66% RH  $A4 > A5$ .
- 5) In the cycles originating at 75 and 85% RH  $A4 \gg A2$  and  $A5 \gg A3$ ;  $A4 \gg A5$  even  $A4 > A1$ .
- 6) The cycles commencing at 32 and 42% RH appear to be uniquely symmetrical inasmuch as changes in relative humidity result in similar SA losses, irrespective of direction.
- 7) Plots of SA values, A1 to A5, as a function of relative humidity (Fig. 5), show that changing humidities below 66% RH result in a converging to a common low value that occurs between 42 and 57% RH.

### Second Series

The results shown in Fig. 6 indicate the following:

- 1) SA lost on exposure to low humidities can be recovered only by exposure to very high humidities.
- 2) As expected, the extent of recovery is inversely proportional to the magnitude of the SA loss (see Fig. 6, plot at lower right).

### Discussion

The good agreement between the results of previous studies (1,4) and the present work leaves little doubt that  $N_2$  BET surface area loss on storage at varying humidities is a reality. Surface area reduction was also observed using water as adsorbate (6), and the phenomenon cannot be considered as an artefact of nitrogen adsorption. Despite the large discrepancies between  $N_2$  and  $H_2O$  BET area in numerical values they appear to be qualitatively similar. Furthermore, the area at 52% RH was only half of that at saturation when examined by the small-angle X-ray scattering method (7), requiring no adsorbate. It suggests that the results reflect real physical changes.

### Rate and Frequency Dependence

The results indicate that SA is affected not only by the absolute level of humidity during storage but also by the number and rate of changes in relative humidity. Hunt et al. (1) observed that crushed specimens undergo smaller SA decrease than do 12 mm diameter cylinders because the former specimens dry faster. An important element of the solvent replacement technique (5) was the very high drying rate that resulted in  $N_2$  SA values comparable to those obtained with water as adsorbent.

It seems quite possible that the SA values below 42% RH in the First Series would, after a number of RH changes, decrease to less than  $10 \text{ m}^2 \text{ g}^{-1}$ .



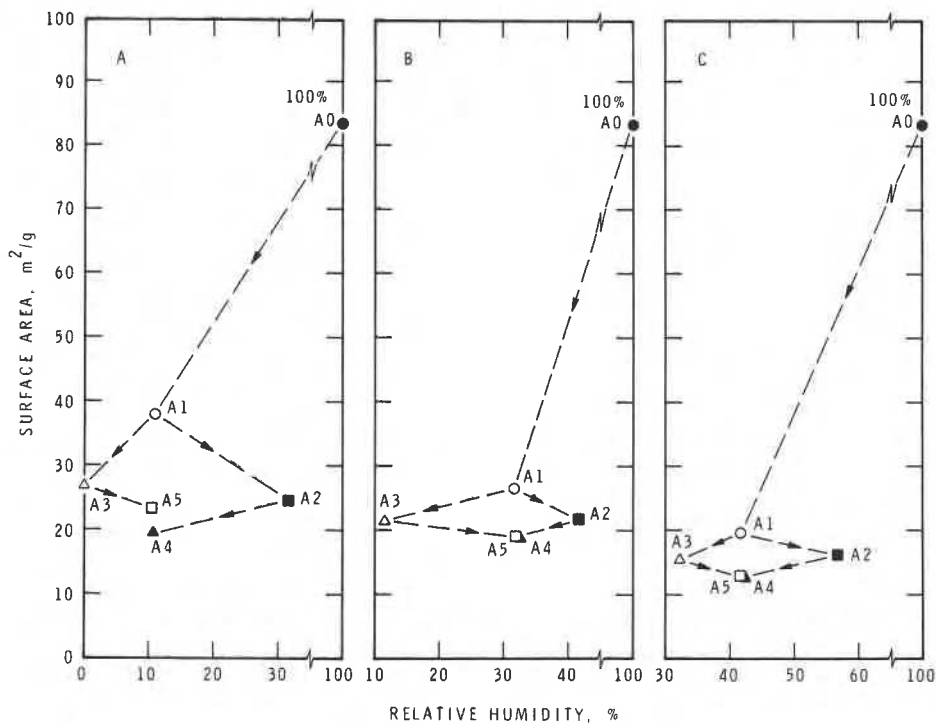


FIG. 3

SA at various stages of conditioning cycle, A0 to A5

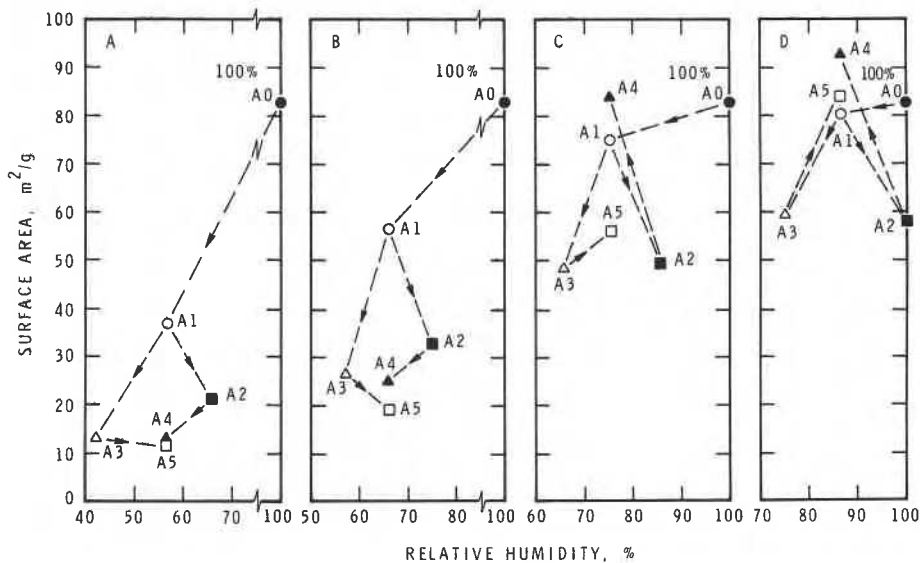


FIG. 4

SA at various stages of conditioning cycle, A0 to A5

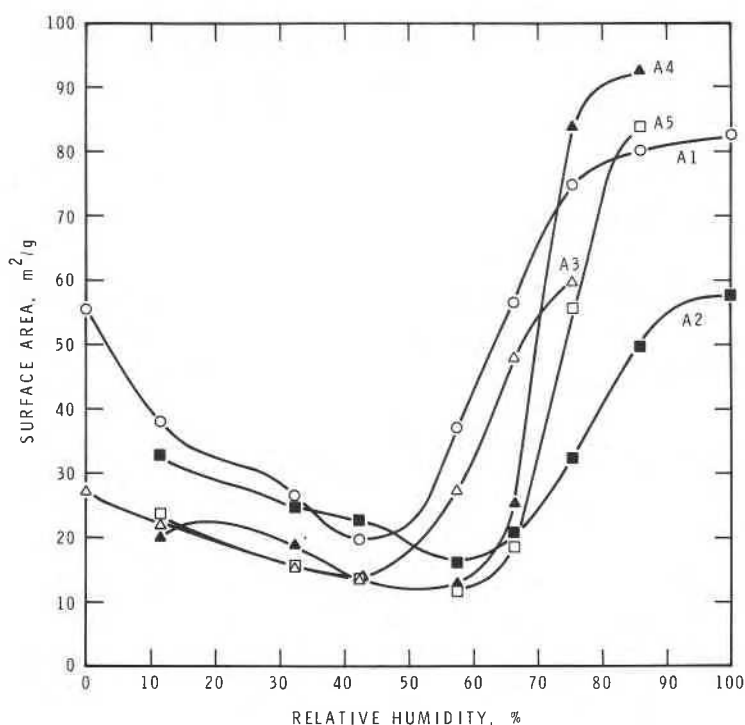


FIG. 5

A1 . . . A5 values as a function of RH

In this region the specimens experience the highest rate of drying if the moist samples are placed in the respective desiccators, minimizing the effects of SA loss. Several subsequent conditioning steps are probably required to reduce SA to its final low value, at which stage the A1 versus RH curve would closely resemble that of Parrott et al. (4).

The rate of drying above 47% RH also affects the ultimate value of drying shrinkage (8) and creep (9-11). Drying at rapid rates induces stresses of magnitude proportional to rate of drying.

Cady et al. (12) observed transient decrease of the tensile strength of cement mortar briquets on drying, and Litvan (13) has reported similar transient reduction of Young's modulus of hardened cement paste. Repeated wetting and drying cycles appear to affect creep of cement paste (9,10) and the volume changes of  $\text{Ca(OH)}_2$  compacts (14).

#### 40 to 60% RH Range

The greatest decrease in SA occurs at or in the vicinity of 40% RH. A relative pressure of 0.4 is of great significance in several areas of surface chemistry. In hundreds of adsorption isotherms, including hardened cement paste, this is the inception point of the hysteresis loop (15,16); below this pressure micropore filling and above it capillary filling occur. For this reason 0.4 relative pressure was chosen as the reference state for surface area determination by the  $\alpha$ -method (17).

It is also known that when dry cement paste is wetted, 65 to 70% of the expansion takes place below 50% RH; and that when d-dried and exposed to higher humidities a potential for irreversible shrinkage develops (18).

Creep rate increases rapidly at humidities above 42% RH (19); the compressive strength of cement mortar and the elastic modulus of cement paste (20), if conditioned at 40 to 50% RH, are at their lowest level. The coefficient of thermal expansion of cement paste is maximum at 40% RH (14).

In first-drying shrinkage 47% RH was found to be a most significant

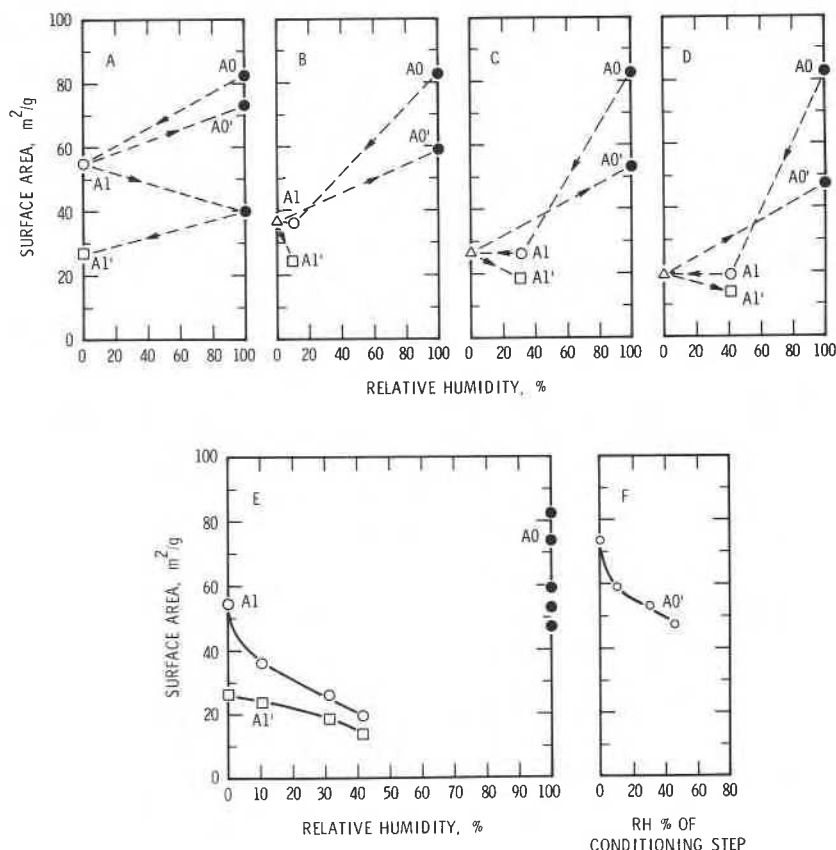


FIG. 6

SA regeneration after conditioning.

Sequence of procedure 100% RH (A0) → X% RH (A1) → 0% RH (A0<sup>1</sup>)

Top graphs: SA at various stages of conditioning.

Bottom, left: A1 and A1<sup>1</sup> vs RH.

Right: A0<sup>1</sup> as a function of RH of A1 conditioning step.

condition; and Helmuth and Turk drew attention to the link between shrinkage and SA loss (8). Feldman showed (21) that, on rewetting, the layers of the cement paste open up significantly only after 42% RH. Shrinkage of lime compacts following carbonation (22) and conditioning at various humidities (14) is maximum at 50% RH.

### Reversibility

Whereas changing humidities during storage, either increasing or decreasing, result in lower surface area values, the trend is reversed on exposure to very high RH, at least to 75% (Fig. 4). Recovery of the SA loss on resaturation in water has been reported previously (4,7). The reversible portion of drying shrinkage manifested itself only on rewetting (8).

### Possible Causes of Aging

A time-dependent alteration of high specific surface area solids is a well known phenomenon (23) attributed to several causes. It will be examined for relevance to the present case of cement paste. First, however, the possibility that the observations can be accounted for by assuming continued hydration has to be considered. Obviously, the formation of new compounds could alter surface area. This hypothesis must be rejected, however, because the bottle hydrated cement used was well hydrated on 0 day. It may be mentioned that hydration, except at high temperatures and for an initial period (24), normally leads to an increase and not a decrease of SA (25).

Surface area loss of high specific SA solids is often a result of enhanced solubility. Such solids are known to decrease their surface free energy through dissolution and precipitation. This mechanism must also be ruled out for cement pastes for the following reasons:

- 1) SA decrease occurs at humidities below 40% RH, yet adsorbed water in this region rejects solutes (26).
- 2) There is least loss of SA at high humidities, when the conditions for this mechanism would be the most favorable.
- 3) On the basis of the mechanism, SA decreases during prolonged exposure to constant humidity, so that insensitivity to RH changes would be expected. The contrary has been observed.

Siliceous surfaces are known to undergo gradual dehydration of the SiOH groups leading to the formation of Si-O-Si bridges, a process accompanied by surface area reduction (27). Polymerization of surface silanol groups as one cause of aging was suggested by Collepardi (28), who also reported that from the rate of SA decrease at different temperatures the activation energy is 10 to 12 kcal/mol. This value is in the same range as the activation energy of the silanol condensation reaction determined by Kiselev (29).

In support of the silanol polymerization theory is the well-established fact that rehydration of dehydrated silica, as for SA change, is a function of relative humidity and will occur only if liquid water is present in the capillaries (30). With this mechanism the difficulty is that the effect of alternating humidities cannot be explained. Recrystallization of one or more constituents on a large scale can be ruled out on the basis of Collepardi's work, which could not detect in the X-ray diffractograms of calcium silica hydrates any change due to aging (28).

Collapse of the layered structure of the silicate hydrates on drying does not explain SA reduction adequately because the phenomenon is observed also at relatively high humidities, and even on wetting (see points A1 and A2 in Fig. 4). For the same reason the suggestion that gel particles are brought closer together during desorption and that contact points are created under pressure (31) cannot be accepted as the full explanation.

The most important characteristics of the SA loss phenomenon that must be accounted for are: 1) the area reduction itself, 2) the sensitivity of the phenomenon to the number and 3) the rate of humidity changes. There is little doubt that first drying shrinkage (8) is an important factor in the initial phases of conditioning, but it cannot account for all the findings.

The observations listed above indicate, however, the operation of a time-dependent process greatly affecting the behaviour of the paste. Under changing humidity conditions two such processes can be identified: moisture transfer, and volume change of the solid. Time dependence of volume change in response to RH change has not, to the authors' knowledge, been reported in

the literature. It seems, therefore, reasonable to assume that the rate-controlling process influencing the events is the transfer of moisture.

This hypothesis implies that decrease in SA follows from the existence of moisture gradient, resulting in turn in non-uniform volume changes throughout the paste. Such a condition deforms the solid network, breaking some bonds and creating new contact points, the formation of which was suggested by Powers (31). The mechanism is a common occurrence with all types of porous solids. The unique feature of hydrated cement paste is that bonds between the surfaces of silicate particles form readily when they are brought into close proximity, as evidenced by the great strength of cold (32) and hot (33) compacted cement.

Loss of SA can arise from reduced accessibility of regions or reduction of the area of the particles involved. Gregg and Langford found (34) silica deformable under compaction and suggested that the particles retain their altered shape even after the newly formed junctions open up to accommodate relative movement of the particles when stress conditions continue to change. If true, this mechanism implies the occurrence of area loss whenever stress, i.e., wetting or drying, deforms the paste.

Because the gradient is a function of the rate of wetting and drying the loss of SA is, understandably, also affected. Interparticle bonds, which appear to be involved in the changes brought about by moisture change in disperse systems such as concrete, are most important. The mechanical properties of such solids are determined more by the strength of the contacts between the particles than by the strength of the particles themselves (35). It is thus to be expected that a phenomenon resulting in diminution of SA also affects creep and drying shrinkage phenomena. Although the cause of SA loss is not clear, there is little doubt that calling the phenomenon "aging" is incorrect. The process is not dependent on time but on change of moisture content and the rate of this process.

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