

A Study of Length Changes of Compacts of Portland Cement on Exposure to H₂O

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The various methods for studying the hydration rate of portland cement are reviewed, with particular reference to volumetric measurements. A new method is described for studying the interaction with H₂O of portland cement and its constituents by following the length change with time of a compact of unhydrated material; the formation and properties of the compacts are also outlined. The advantages of this method are discussed, the chief being that the particles of unhydrated cement are in direct contact with one another; this enables the length change to reflect immediately the formation of hydrated products at the particle boundaries and the study of hydration reaction and other effects within the first seconds of wetting. Sample size of the order of 1 by 0.25 by 0.06 in. allows close temperature control and the possibility of a study of vapor phase hydration is cited as a further advantage. Results of length changes are presented for vapor phase exposure at 20, 50 and 85 percent RH. Results are presented also for liquid phase hydration, including observations made only one minute after the start of hydration and including the effect of pre-exposure for periods from 5 min to 5 days at the three humidities on subsequent liquid phase hydration. The experiments showed that expansion begins immediately on exposure to water (liquid or vapor) and continues with time and that pre-exposure of the specimens even at low humidities has an effect on subsequent hydration rates. The meaning of "setting" and "hardening" with regard to compacts is discussed.

•THE HYDRATION rate of portland cement has been studied by many methods, one of these being the strength development of concrete as a function of time. Other methods include the microscopic examination of pastes and X-ray diffraction analysis of the unhydrated cement in hardened pastes. Whereas the latter method may eventually be best for measuring the rate of hydration of the individual phases, other techniques will always add to the knowledge concerning the mechanism of hydration. These techniques, listed as indirect methods (1), are concerned with the measurement of a change in the physical and chemical properties with time. Among these are the evolution of the heat of hydration, the change in the non-evaporable water, the development of specific surface, and the formation of calcium hydroxide. The volume change method, in addition to being a valuable adjunct to other methods, has some advantages because it reflects not only the chemical, but also the physical, changes.

VOLUME CHANGE METHODS

When portland cement is in the presence of water, the chemical and physical changes that occur are accompanied by a reduction in the total absolute volume of the system. This was shown first by Le Chatelier (2) and later by Kuhl (3) and has also been shown for other hydrating systems (4). Le Chatelier also observed the apparent volume increase of the solid during hydration as made evident by the bursting of the inclosing vessels. A. H. White (5) reviewed the considerable experimental work (6, 7, 8, 9) done before 1915 on measuring the volume changes of neat cement and concrete bars. The results of this work showed that cement expanded continuously when kept in water and contracted markedly when maintained in air. This early work led to volume change studies which may be divided according to three methods:

1. Measurement of absolute volume change of the system by the dilatometer,
2. Measurement of apparent volume change of solids, and
3. Measurement of the sedimentation rate of paste and mortars.

Method 1 was refined by a succession of workers (2, 4, 10, 11) and was applied to plaster of paris, various types of portland cement, the effect of additives on portland cement, and gelatin. Although a good relationship between heat of hydration and volume decrease for portland cement was not obtained, a measure of the rate of hydration was found, including the effect of gypsum as the retarder.

Much of the work relating to Method 2 has been standardized (12) and applied to study of apparent volume change from the aspect of volume stability (13). In his investigations of varying compositions of free lime, magnesia, reactive silica in portland cement and various clinker compositions, Bogue (14) did, in effect, study the magnitude and rate of hydration of some of these components in cement. This volume change work extended into autoclave reactions, alkali reactivity of cement aggregates, and sulfate resistance of cements (15). More success in correlating volume change with reaction rate was obtained by L. Chassevent (11) for the plaster of paris system and recently in this laboratory for plaster of paris (16) and lime (17). Where the study dealt with a single chemical compound, the success was understandable as compared with multicomponent systems.

Method 3, used mainly by Powers (18) and Steinour (19), indicated that the size, shape, and number of cement particles are not altered appreciably by the reactions occurring within the first hour or so after contact with water. This method produced important physical evidence in opposition to the theory of Baikov (20) and Rehbinder (21) that at early hydration times, the cement particles are dispersed or "colloidized." As pointed out by Powers (22), the evidence on which the theory was based, the rapid development of area at early hydration times, may be explained by the thin layer of gel on the unhydrated cement particles.

In the development of the new volume change method, an attempt was made to overcome some of the chief limitations of the previous methods for measuring the apparent volume change, e.g., control of the temperature throughout the mass of the sample during hydration, and the ability to measure the length change from the moment the water comes in contact with the solid. This method affords the added feature of observing volume change when cement is hydrated with water in the vapor phase.

A NEW VOLUME CHANGE METHOD

It has been shown (23, 24) that dry, powdered, inorganic materials, such as calcium carbonate, silica, plaster of paris and calcium oxide (17), can be compacted to produce rigid porous bodies; further, these bodies can be used for the study of their length change isotherms. Compacts of unhydrated portland cement have now been produced and their length changes were measured during the period of hydration.

Materials

The cement used was a Type I with the chemical and physical properties shown in Table 1. It was obtained directly from the plant and stored in small sealed containers

in desiccators over magnesium perchlorate. The extent of carbonation is indicated in Table 1.

Experimental

Fabrication of Compacts. — The compacts were fabricated in a mold 1.25 in. in diameter, care being taken to insure that the material was evenly distributed so that the load could be evenly applied. Compacts were produced under pressures varying from 8,150 to 118,000 psi. The entire procedure was performed in a dry box using magnesium perchlorate (anhydrous) as a drying agent; it was found that the relative humidity in the box was maintained well below 1 percent. Sufficient material was compacted to give a final thickness of 0.06 in. and a specimen of rectangular shape, approximately 1 by 0.25 in., was cut from it. The sample normally weighed less than one gram.

Extensometer and Hydration Cell. — Because of the small sample size, an accurate means of length change measurement had to be used. This was achieved by a modified Tuckerman gage extensometer (Fig. 1). This optical instrument measured the length change with an accuracy of 2×10^{-6} in./in. The sample (1) was held against the knife edges (2 and 3) by a light spring (4), the sample resting on a holder (5). The optical system consisted of a fixed mirror (6) and a tilting mirror (7) which was one face of the rocking lozenge. The whole assembly was supported by a stand. The final assembly remained in the dry box during and after mounting of the sample on the extensometer and then was carefully placed in the hydration cell. This cell (Fig. 2) is made so that the sample can be subjected to high vacuum; ground glass joints and valves are used in its construction to exclude CO₂. The cell is provided with an optical window through which the extensometer can be read. A pipette arrangement is used for injecting water at a controlled rate when hydration in the liquid phase is to begin. Excess water may also be withdrawn from the sample when required.

When the sample and assembly are placed in the cell, the optical window assembly is placed on the ground joint (4) and the valve (2) is opened to vacuum (Fig. 2). After evacuation the cell is removed from the dry box and placed in a temperature controlled bath.

Measurement of Length Change as Function of Hydration Time. — The measurement of length change during the vapor phase exposure of the compact can be achieved at any desired humidity by joining the cell through the ball and socket joint to a vacuum system; from this system water vapor at any desired humidity may be obtained. Because this exposure proceeds with the exclusion of all gases except water vapor, the diffusion rate of the vapor is rapid and the desired humidity is attained quickly.

TABLE 1
ANALYSES OF UNHYDRATED PORTLAND CEMENT

Analysis	Percent
Chemical:	
CaO	63.1
SiO ₂	20.8
Al ₂ O ₃	5.1
Fe ₂ O ₃	3.5
MgO	1.5
SO ₃	2.2
Na ₂ O	0.8
K ₂ O	0.7
Free lime	0.5
CO ₂	0.14
Potential Mineralogical:	
C ₃ S	50.9
C ₂ S	21.4
C ₃ A	7.5
C ₄ AF	10.5
Physical:	
Blaine surface area	= 3,240 sq cm/gm
Autoclave expansion	= 0.01 percent
Initial set Vicat	= 3 hr 45 min
Initial set Gillmore	= 3 hr 30 min
Final set Gillmore	= 5 hr 15 min
Compressive strength:	
at 3 days	1,445 psi
at 7 days	2,617 psi

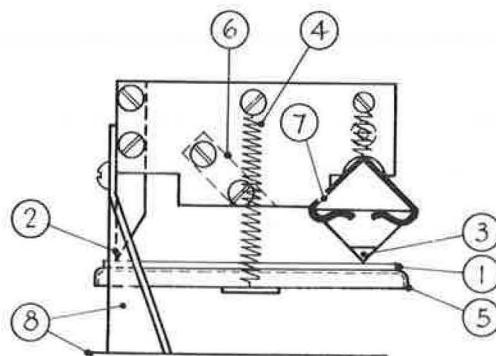


Figure 1. Extensometer.

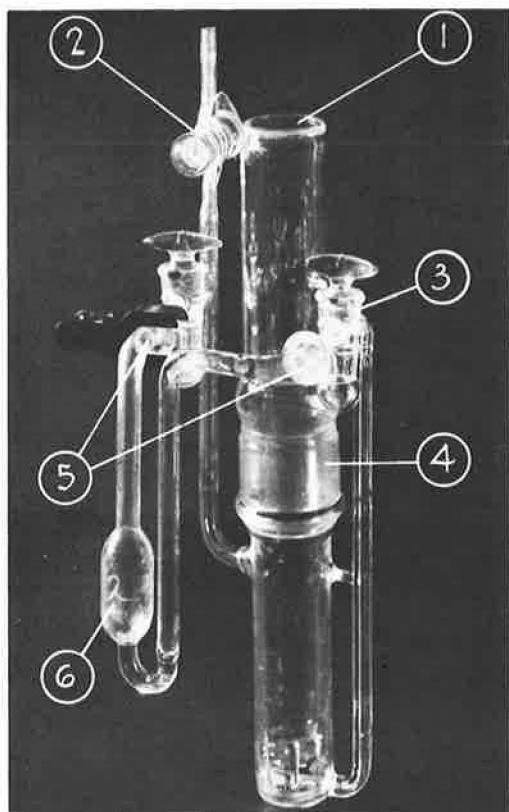


Figure 2. Hydration cell (1, optical window; 2, valve to vacuum; 3, controlling valve; 4, large ground glass joint; 5, ball and socket joint; 6, pipette).

Liquid phase hydration is also achieved without exposure of the sample to air. The pipette containing liquid water is placed on the joints (Fig. 2); the assembly is then placed in the constant temperature bath until the pipette has reached bath temperature. Water is then injected by the controlling valve (3) until the sample is entirely immersed. This procedure is completed in 15 sec, after which readings of length change begin. After a given time, the level of the water is lowered below the level of the sample by admitting some air into the cell.

Results

Mercury Porosimetry.—Plots of void fraction against the logarithm of the compaction pressure have yielded characteristic linear relationships for several materials (23, 25) and this is also observed for the unhydrated cement used in these ex-

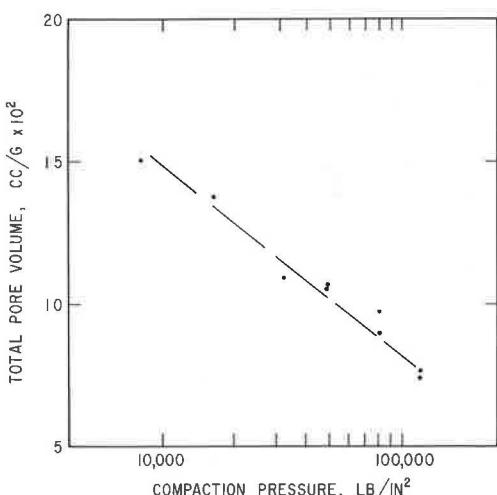


Figure 3. Relationship of total pore volume vs compaction pressure for unhydrated cement.

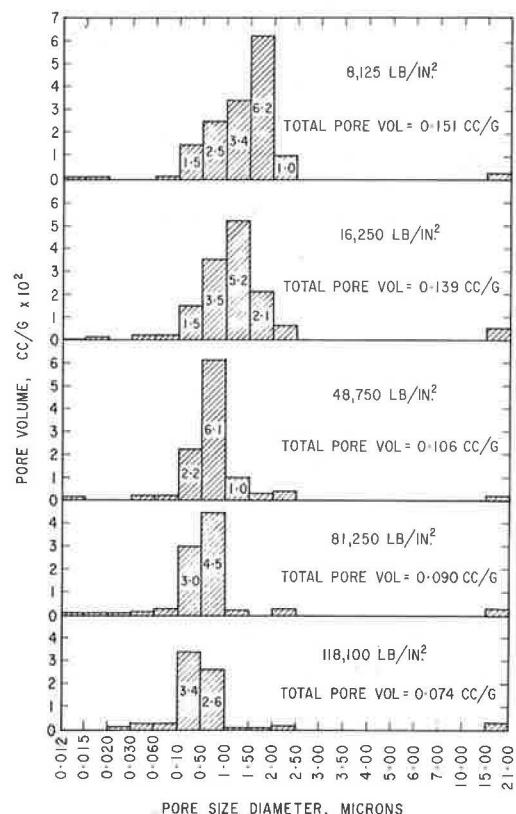


Figure 4. Effect of compaction pressure on pore size distribution and pore volume of unhydrated cement.

periments. Figure 3 is a plot of this relationship for compaction pressures varying from 8,150 to 118,000 psi. Mercury penetration results shown in Figure 4 illustrate how the pore size distribution is changed and the pore volume is lowered with increasing pressure of compaction.

Vapor Phase Exposure. —After initial degassing, during which only slight contraction was observed, vapor phase measurements were taken at three relative humidities: 85, 50, and 20 percent on compacts formed at 49,000 psi. Although readings were taken after 1 min, it was observed that an expansion began on exposure of the sample to water vapor.

For each humidity, the high initial rate of expansion was followed by a continually decreasing rate reaching a negligible value after 5 days, when the experiments were terminated. The higher the humidity, the greater was the initial rate of expansion and the final value for the expansion. The curves in Figure 5 are the mean values obtained from 10 to 30 experiments showing the general characteristics. Results varied somewhat depending on the bottle of unhydrated cement used even though from the same batch; deviation from the mean at each humidity was as much as 20 percent. It was observed, however, that expansions attained mean values of approximately 0.14, 0.08, and 0.05 percent after exposure to 85, 50, and 20 percent RH, respectively. The reproducibility is thus good enough to make the differences at the various humidities significant.

Liquid Phase Hydration. —Results were obtained for the expansion of the compacted specimen as a function of time from the first minute after they were submerged in water at 70 F. These results and those for samples subjected to pre-exposure to water vapor are included in Figures 6, 7 and 8. Although the expansion rate decreased with time, a measurable rate was observed for as long as measurements were taken (12 days). Expansion of up to 0.30 percent was obtained within a 24-hr period.

Effect of Vapor Exposure on Expansion Due to Liquid Phase Hydration. —Results showing the effect of pre-exposure at 85, 50, and 20 percent RH for times of approximately 5 min, 6 hr, 24 hr and 5 days are shown in Figures 6, 7, and 8. Rates are very much reduced for the 85 percent humidity curves and for the 5-day exposure the rate of expansion is almost negligible. Even for the 5-min exposure the rate was considerably reduced, indicating considerable interaction at so short a time. At 50 percent RH, results still indicate a considerable interaction, although to a much less extent than at 85 percent; exposure for 5 min at 85 percent will reduce the initial rate (length change for

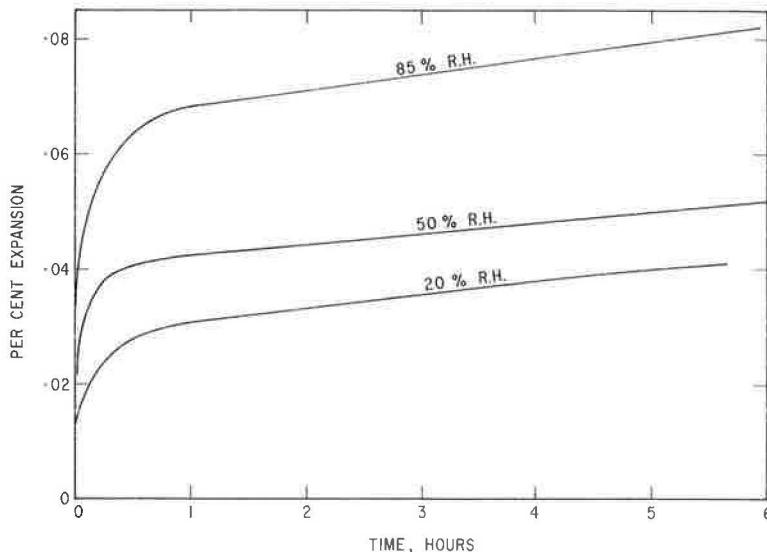


Figure 5. Expansion during exposure to various humidities.

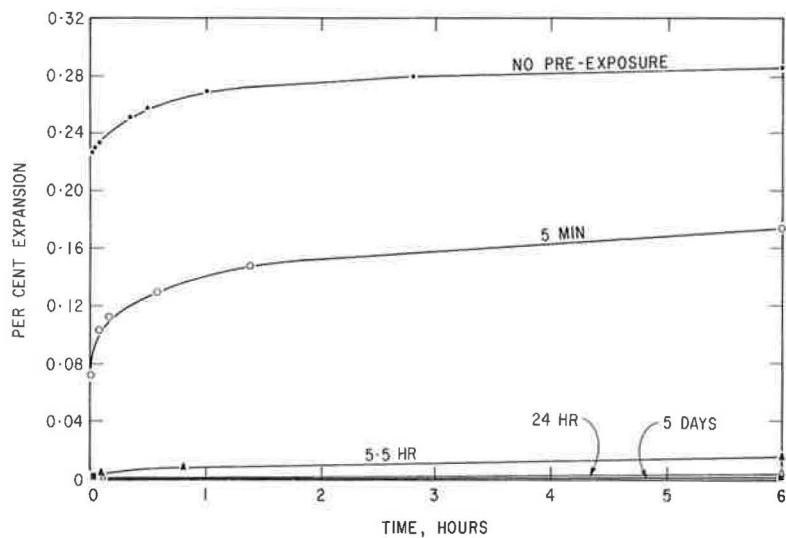


Figure 6. Expansion during submersion of cement pre-exposed to 85 percent RH for various time intervals.

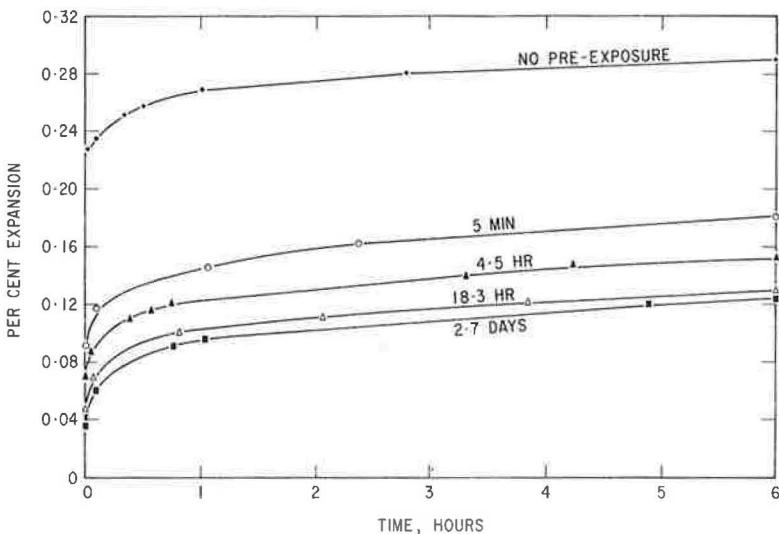


Figure 7. Expansion during submersion of cement pre-exposed to 50 percent RH for various time intervals.

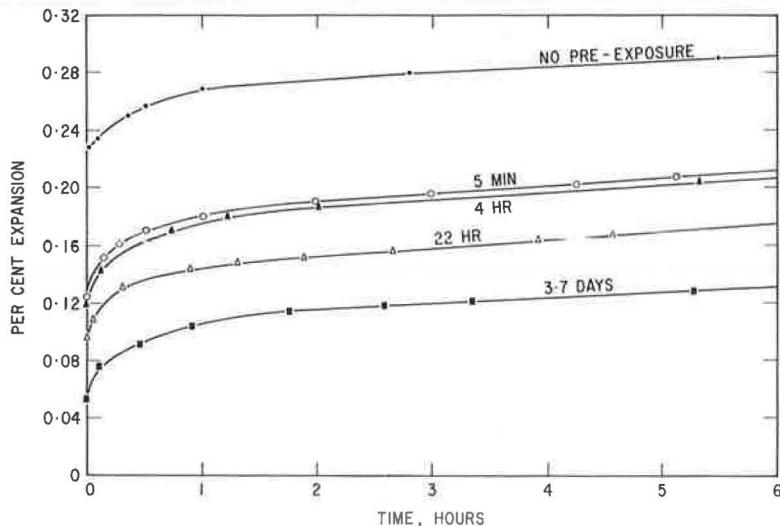


Figure 8. Expansion during submersion of cement pre-exposed to 20 percent RH for various time intervals.

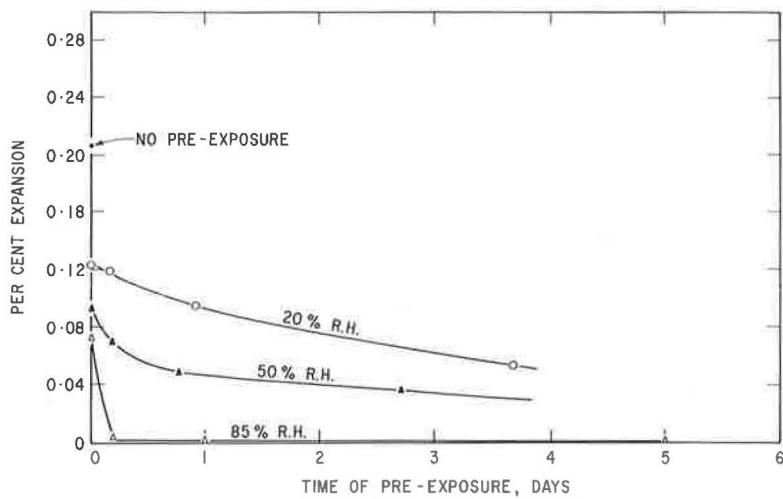


Figure 9. Expansion after first minute of submersion vs pre-exposure time to various relative humidities.

the first minute) as much as at 50 percent for 5 hr (Fig. 9). Continued exposure at 50 percent for greater than 5 hr does not greatly alter the initial rate of expansion. This is also indicated by the results of the vapor phase hydration (Fig. 5). Results of exposure at 20 percent RH show a similar trend. It is significant, as shown by the vapor phase results, that there is considerable interaction at such low humidities between the water vapor and the unhydrated cement.

The results obtained from submerging samples in water are reproducible for the samples that were pre-exposed for 5 hr, 24 hr, and 5 days at 85 percent RH. For the samples pre-exposed for 5 hr at 50 percent RH, the value of the expansion at 1 min may vary by 15 percent, whereas those pre-exposed at the same time at 20 percent humidity may vary by about 30 percent. If, however, samples were taken for which the results for vapor hydration did not vary more than 10 percent, the reproducibility of results of liquid phase hydration was within 10 percent. Although the cement may be affected to different degrees by the moisture and CO_2 contamination, the possibility of a variation of the clinker composition from sample to sample is very real. This is a disadvantage in using small samples. Despite these difficulties, the trends shown are considered to be significant.

Discussion

Pore Structure of Compact. —It has been shown (26) that the compaction behavior of powders depends markedly on their hardness and that their results are described by two nearly independent probabilistic processes. The first is the filling of holes of the same order of size as the original particles. This occurs primarily by particles sliding past one another, which may require slight fracturing. The second process is associated with the filling of voids substantially smaller than the original particles by plastic flow or by fragmentation. This process, however, does not add significantly to the surface area of the material (25). The pore structure of the compact is quite reproducible and, as shown in Figures 3 and 4, may be defined by the compaction pressure. The strength and rigidity of this body is probably derived more from physical than chemical forces, and as shown by Czernin (27), compacted bodies can develop fair strengths.

The compact, with its particles in direct contact and its natural rigidity, possesses the primary structure from which the final structure is developed on hydration (28, 29). The important characteristic is that it possesses this structure before any contact with water, and the effective water/cement ratio will be defined by pore volume of the compact.

Control of Conditions. —Because of their size, these bodies can be made in controlled humidity conditions and experiments can be performed in vacuum. Temperature control can be easily maintained externally but it is within a sample that control is difficult. The hydration of cement is an exothermic reaction and unless the heat can be removed rapidly from the site of the reaction, the temperature will rise. The likelihood of this happening depends on the mass of the sample for the quantity of heat liberated and on the thickness of the sample for the rate of heat transfer from within. Optimum conditions are achieved in this method by having a very thin sample; this is not usually possible in any of the other volume change methods.

The use of small samples also has the advantage of avoiding gradients of stress. When using large bars in the test, although of greater practical importance, the volume changes would not correctly reflect the progress of a reaction. Volume change gradients through the larger body can cause decrease in strength, and finally, destruction of the body.

Measurements at Early Times. —The primary advantage of this method is the ability to observe within the first minute the volume change when water comes in contact with the unhydrated cement particles. The sample is under vacuum when water is injected and this fosters the rapid distribution of water in the pores and consequent rapid wetting of all the surface. Because the particles are in contact with each other, any physical changes in the particles due to reaction will be reflected as an apparent volume change of the system. For these reasons the measurement of length change of a compact should reflect the rate of reaction without any lag in time.

Cement paste, as is used in the other volume change methods, is formed during several minutes of mixing and handling; it is a plastic cohesive mass composed of an

aqueous solution and particles of clinker. Owing to the nature of the paste, molding techniques were used and sometimes, in the mortar bar methods, readings were not taken till 24 hr after the initial wetting. In other methods, however, readings were taken after 15 min or less; in the sedimentation technique, the time may be less.

The primary structure of cement paste is the network of discrete particles formed by the process of mixing the particles with water. These particles are separated from each other by water and until they come into contact with each other, an expansion due to initial formation of hydrate product on the surface of the particle cannot be observed. In fact, it has been reported (29) that the earliest time at which an expansion has been observed in portland cement paste is 1½ hr after mixing. Measurements in air of volume changes of normally mixed pastes have shown marked and extended contractions from early ages. Thus, no volume change representing the formation and movement of the hydrated product from the first instant of wetting can be made by other methods for liquid phase hydration.

Vapor Phase Exposure. —Measurement of volume change during vapor exposure can only be made by this method. The cement particles must never come into contact with water before the study, and the primary structure must not only be established but must be represented by particle contact so that the limited hydration which may take place can be detected and measured. This direct contact of the cement particles avoids all contraction during vapor phase exposure even at low humidities.

The discussion of primary structure and particle-to-particle contact leads to the subject of the "setting" or "hardening" of cement. As was pointed out by Steinour (30), these terms arose from practical considerations and are not theoretical. Nevertheless, there has been some debate as to the difference in the nature of the hydration process before and after setting. When the terms are applied to the hydration of compacted portland cement, one is forced to conclude that setting has taken place before hydration has begun or at least within a few minutes after exposure to water.

Study of Effect of External Agents or Additives. —The effect of retarders or accelerators on early hydration can be followed by volume changes in a similar manner as by the other methods: either by mixing the additive with the unhydrated cement powder or by dissolving it in the water to be introduced to the sample.

Greater versatility is obtained in this method, however, in the study of external agents. Effect of carbonation from the gas phase can be studied during vapor phase exposure with confidence of attaining uniform carbonation throughout the sample.

Interpretation of Results. —The initial expansion of the unhydrated cement compact may be attributed to the phenomena of stress relaxation, dispersion on wetting, physical adsorption, and hydration of the cement particles. It can be expected that dry powders when compacted should be found in a state of stress and that this stress may be relaxed through irreversible expansion when the body is wetted by liquids. Cyclic wetting by organic liquids, such as methanol, for similar systems did not result in irreversible expansion, thus indicating that the residual stress is negligible for the pressure ranges used in these experiments.

Compacts of some materials disperse when immersed in water. Such compacts, however, will behave as rigid bodies up to high humidities as was shown (23, 24) for compacts of calcium carbonate. For plaster of paris it has been found (16) that a small amount of hydration on the particles by exposure to vapor will prevent any disintegration on submersion in water. Compacts of unhydrated cement, even without exposure to vapor, show no tendency to disperse when immersed in water.

There is no doubt that some expansion will occur due to physical adsorption; at 20 percent RH, expansion may be due entirely to this, because some previous work (31) has suggested from measurements of "evaporable and non-evaporable water" that no interaction other than physical adsorption takes place at this humidity. The concept of "evaporable water," however, is somewhat arbitrary as far as an absolute definition of physically or chemically sorbed water is concerned. The amount of reaction product formed at 20 percent RH in all likelihood would be very small and may not be of the same nature as in liquid phase hydration; some form of chemisorption may be occurring. The formation of small quantities of hydration product formed on the surface of each particle may be sufficient to be detected by this technique.

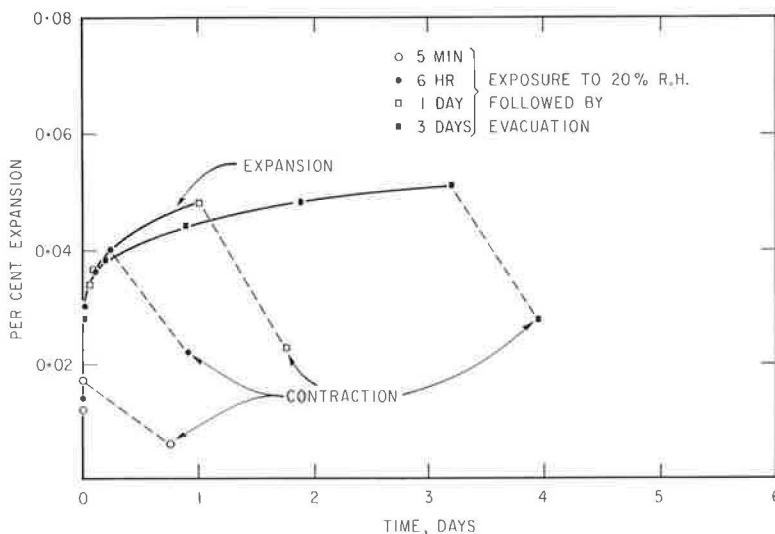


Figure 10. Expansion on exposure to 20 percent RH and contraction on evacuation.

The evidence for considering that chemical interaction takes place at 20 percent RH is:

1. Expansion occurred continuously, although at a decreasing rate for as long as observations were taken (5 days); this is illustrated in Figures 5 and 10 and presented in the results; for physical adsorption at low humidities, equilibrium is attained in a few hours.

2. Vapor phase exposure affects subsequent liquid phase exposure (Fig. 9); this must be attributed to chemical reaction because physical adsorption could not have this influence and water vapor pre-exposure was carried out in a high vacuum apparatus where CO_2 effects would be eliminated.

3. Expansion due to physical adsorption was observed (23) on compacts of various materials including precipitated calcium carbonate of particle size 2 to 5 μ ; expansion at equilibrium when exposed to 20 percent RH was 0.018 percent. The particle-size distribution of the unhydrated cement, although varying between 1 to 50 μ , is such that the majority of the particles is about 10 μ . Physical adsorption could not be expected to produce a large expansion under these conditions but if a small quantity of hydrate product was already formed on the particles, a significant expansion would be expected. If this is the case, however, the sample must possess adsorbed water in equilibrium with the humidity where hydration can no longer occur (30 percent RH) and this sample on evacuation should produce contractions greater than those observed on subsequent exposure to 20 percent RH. On evacuation before exposure, contraction was in the order of 0.002 percent.

4. Results obtained by exposing four different samples to 20 percent RH for 5 min, 6 hr, 1 day, and 3 $\frac{1}{4}$ days, respectively, are shown in Figure 10. These samples were evacuated at high vacuum until no further contraction occurred. The time required for this was usually 24 hr. It is observed that after evacuation the sample remained substantially longer than the original length. The irreversible portion increased with time of exposure. This is consistent with the assumption that some chemical interaction is taking place during exposure to 20 percent RH, producing a high surface area product, the formation of which causes an irreversible expansion. As more high surface area product is formed, however, more contraction should occur on drying due to its higher surface area. If this effect was due to physical adsorption, the expansion should be reversible for all exposure times.

The concept of hydration occurring at low humidities is not new. Calcium oxide has been shown to hydrate completely at humidities as low as 20 percent (17, 32) and the presence of a "liquid phase" has been considered unnecessary due to the possibilities of "direct" or "solid-state" mechanisms. Several authors (33, 34, 35) have discussed the possibility of this mechanism and even at 50 percent RH this may be operative because capillary water would not exist at this humidity: the samples were evacuated before exposure and, thus, are on the "adsorption" part of the isotherm.

A portion of the expansion taking place on exposure of the unhydrated cement compacts to vapor is thus considered to be due to hydration. The vapor interacts with the unhydrated cement particles on the external surface, causing a pressure on the next particle due to growth of the hydrate product outward. Hydration may also take place within small cracks in the individual particles, causing each particle to expand individually; this may more easily explain the immediate expansion of the particles on exposure to vapor.

The initial expansion occurring on submersion of the compact in water may be due to both hydration and partial relaxation of the compacts. The hydration that is presumed to take place on vapor phase exposure even at 20 percent humidity, however, and the effect of reduction of the expansion rate on subsequent submersion indicates that the hydration product surrounds the particles with rapid setting of the cement taking place even in the vapor phase. The fairly high rate of expansion for the first minute even on vapor phase exposure leads to an expectation of a high expansion rate for the submersion experiments. It is concluded that the high expansion in the first minute of submersion even for samples without pre-exposure to vapor is due predominantly to hydration from the surface of the particles. This rapid initial expansion may be correlated to the rapid heat evolution that has been observed during the first few minutes of the hydration of cement (36).

The fact that hydration appears to proceed even at low relative humidity but at a decreasing rate with time indicates that products form an effective layer around the unhydrated material. At a higher humidity, the hydration may proceed further. This behavior differs from that of calcium oxide which hydrates completely in the vapor phase, though at a lower rate than in the liquid phase. This occurs even at relative humidities below 20 percent (17).

In the liquid phase, the rapid initial expansion, with decreasing rate, does not explain the dormant period and reacceleration observed by calorimetric measurements during early hydration (36). The fact that the effective water/cement ratio of the compact is approximately 0.10 may provide an explanation. Cement is a complex mixture of different compounds, however, and not until the behavior of each of them can be studied by this method can any interpretations involving the mechanism of hydration and the method of transport of the hydration product be made.

CONCLUSIONS

1. This method provides a means for following both by vapor and liquid phase the immediate formation of hydrated product at the surfaces of cement particles. Owing to the small size of the samples, control of conditions may be exercised.
2. Cement compacts appear to hydrate and expand immediately when exposed to relative humidities as low as 20 percent. No contractions are observed on vapor phase hydration of cement compacts.
3. Pre-exposure to water vapor has a considerable retarding effect on subsequent liquid phase hydration and this effect is a function of both relative humidity and exposure time.
4. Expansion due to liquid phase hydration of compacts begins immediately on wetting and continues at a decreasing rate for at least 12 days.

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