

Behavior of Cements and Related Materials Under Hydrostatic Pressures up to 10,000 Atmospheres

C. E. Weir, C. M. Hunt, and R. L. Blaine

Compression studies were made on hardened cement pastes at 21° C and at pressures as high as 10,000 atmospheres. The effects of composition, age, moisture content, and water-cement ratio were studied. Compressibility of dried portland cement pastes appeared to proceed through a maximum with increased cure, the existence or location of the maximum being dependent on the water-cement ratio. Compression of both portland and aluminous cements increased with increasing evaporable water content. Portland cements with evaporable water contents in the range 17.5 to 32.4 percent exhibited a transition between 2,000 and 3,000 atmospheres. No similar effect occurred in aluminous cement. Experiments indicated that the transition was attributable to hydrated lime formed in the portland cement. Average compressibilities of dried paste were 3.1×10^{-6} and 2.2×10^{-6} atm⁻¹ between 1 and 5,000 atmospheres and between 5,000 and 10,000 atmospheres, respectively. Compression studies were also made with wet silica gel, hydrated tri-calcium silicate, and dry and wet calcium hydroxide.

1. Introduction

In considering studies of the pore-size distribution in hardened cement pastes by the mercury porosimetry techniques [1, 2, 3]¹ data are required on the magnitude of the compression of the cement when subjected to hydrostatic pressures. Normally the compression of the cement paste would be considered negligible, but a study by mercury porosimetry of the extremely small pores believed to exist in dried cement paste would require rather high pressures at which the change in volume of the paste might well be of significance.

Search of the literature revealed that while the elastic properties of concrete have been studied extensively, the measurements were conducted almost exclusively at low pressures and only rarely on neat cement [4]. However, the elastic properties of the rocks and minerals that may be used as aggregates in concrete have been investigated widely even at extreme conditions of temperature and pressure, primarily because of geological interest. The latter data have been compiled by Birch [5].

Because concrete is subjected to moderately high compressive stresses in many commercial applications it appears that there is little direct evidence—aside from successful usage—that the aggregate and the neat cement are compatible as regards compressibility. In order to obtain direct evidence on this question, as well as to evaluate the corrections required in high-pressure mercury porosimetry studies, preliminary data were obtained on the compression of hardened cement pastes with available high pressure equipment. These data immediately showed evidence of a transition at elevated pressures in wet cement and indicated the desirability of a detailed study of the compressibility of cement itself, irrespective of any immediate significance of the data in direct applications.

This paper contains the results of studies of the compression of neat cement pastes at pressures as high as 10,000 atm. Studies were made on the effects of cement type, water-cement ratio, water content, and length of cure. The compression characteristics of several pure materials of interest in connection with cement were also studied.

2. Experimental Method and Preparation of Specimens

2.1. Compression Measurements

The apparatus, experimental technique, and method of calculating the data have been described in detail [6]. An experiment consists in forcing a leakproof piston into the smooth bore of a high-pressure vessel containing the specimen immersed in a light petroleum distillate (Varsol). Readings of the depth of penetration of the piston are made at each 1,000 atm by means of a sensitive dial gage fastened to the piston, pressure in the vessel being measured by means of a calibrated manganin resistance gage immersed in the distillate. The apparatus was calibrated with steel bars having volumes similar to those of the specimens. The compressibility of steel has been measured by Bridgman [7]. The compression is defined as $-\Delta V/V_0$, where V_0 is the volume of the specimen at 1 atm, and ΔV is the change in the volume reckoned from the fiducial pressure of 2,000 atm; compressions at lower pressures, therefore, appear as negative values. All measurements described here were made with decreasing pressures, and frictional forces at the packing on the piston prevented the attainment of reasonable accuracy at pressures much below 2,000 atm. Values of compression reported at 1 atm are not experimental but are obtained by successive approximations. Values of V_0 were obtained by weighing in air before compression measurements and by hydrostatic weighing in distillate after the measurements.

¹ Figures in brackets indicate the literature references at the end of this paper.

2.2. Preparation and Treatment of Specimens

Test specimens were made by casting cement paste in paraffin-coated paper molds designed to yield a cylindrical specimen $\frac{1}{2}$ in. in diameter and 4 in. long. Specimens were removed from the molds after 24 hr and cured at 21° C over water in closed glass containers. Cured specimens were dried in a vacuum at room temperatures with a dry-ice trap interposed between the specimen and the pump in an apparatus similar to that described by Copeland and Hayes [8]. During the initial 24 hr the drying was carried out at a pressure of approximately 1 to 2 mm of Hg. Following the initial 24-hr drying period, further drying was conducted at approximately 2×10^{-3} mm Hg. Cylindrical test specimens prepared in this manner were immersed in dry distillate until evolution of displaced air appeared to cease and were then subjected to a short evacuation at a pressure sufficiently low to cause the distillate to boil at room temperature. The resulting vacuum-impregnated specimens were used for test.

Certain materials studied could not be cast conveniently in cylindrical form. Such materials were packed into a thin-walled steel cylinder, which was open at one end, having dimensions $\frac{1}{2}$ in. in diameter and 4 in. long. The material was impregnated with distillate, as previously described, prior to test.

2.3. Materials Studied

The materials studied included portland and aluminous cements, silica gel, tricalcium silicate, and calcium hydroxide.

a. Cements

The portland and aluminous cements studied in greatest detail had the compositions shown in table 1. The portland cement was denoted as cement A. This was a type-I (Federal Specification SS-C-192a) cement ground from clinker, the composition of which is given in the table. Limited studies were also conducted on other portland cements meeting the requirements of Federal Specification SS-C-192a for types I, II, III, IV, and V.

b. Silica Gel

The silica gel studied contained 205 percent of evaporable water, based on the dry weight of the sample. An additional 5.4 percent of water was removed by ignition at 1,000° C for 15 min. After an overnight evacuation at 100° to 110° C, the surface area of the material by low-temperature nitrogen adsorption was 749 m²/g. This is a rather large surface area even for silica gel.

c. Tricalcium Silicate

The tricalcium silicate was prepared by heating and reheating of an intimately mixed paste of calcium carbonate and silica gel.

d. Calcium Hydroxide

The calcium hydroxide used was a reagent-grade product obtained commercially.

TABLE 1. Compositions of cements studied

Cement A ^a (portland cement, type I)			Aluminous cement	
Oxide	Percentage by weight	Calculated composition, percentage by weight	Oxide	Percentage by weight
CaO.....	65.13	3CaO·SiO ₂ , 56%.....	CaO.....	36.8
SiO ₂	22.62	3CaO·Al ₂ O ₃ , 3%.....	SiO ₂	8.6
Al ₂ O ₃	4.41	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃ , 16%.....	Al ₂ O ₃	42.7
Fe ₂ O ₃	5.33	2CaO·SiO ₂ , 23%.....	Fe ₂ O ₃	4.3
SO ₃	0.10	-----	SO ₃	0.3
MgO.....	1.71	-----	MgO.....	.8
Na ₂ O.....	0.04	-----	FeO.....	6.2
K ₂ O.....	.28	-----	TiO ₂	0.4
Loss on ignition, ^a	.37	-----	Gain on ignition,	.1
Insoluble residue.	.14	-----	Insoluble residue.	1.7

^a This is an analysis of clinker that was interground with different amounts of gypsum and blended to 1.8 percent of SO₃. Ignition loss of blended cement was 1.69 percent.

2.4. Determination of Volume and Cement Content of Specimens

The specimens were weighed in air before test and weighed in distillate after completion of the compressibility measurements. The volumes of the specimens at 1 atm, V_0 , were calculated from the relationship

$$V_0 = \frac{w - w_v}{d_v}, \quad (1)$$

where w is the weight of the specimen in air, w_v is the weight of the specimen in distillate, and d_v is the density of the distillate.

The specimens were finally ignited in platinum crucibles at 1,050° C for 15 min, after first burning off the distillate in a flame. The cement content of the specimens, C , was calculated from the relationship

$$C = w_i(1 + i), \quad (2)$$

where w_i is the ignited weight of the hydrated specimen, and i is the fractional ignition loss of the original cement.

3. Results and Discussion

3.1. General Considerations

Prior to a discussion of the experimental results it is advisable to consider details of the experiments that affect the experimental accuracy and the rigor with which the experimental data may be treated.

In many measurements on porous materials the failure to remove all air from the voids may introduce serious errors. However, in these studies the specimens were impregnated with distillate at reduced pressures. Under such conditions, if the whole void volume contains air trapped at the reduced pressure, the volume of the air at 1,000 atm will be quite small. Of still greater importance is the fact that the change in volume of the trapped air between 10,000 and 1,000 atm will be expected to produce a negligible error in these measurements. Two other factors tend to further decrease this small error. First, a large

quantity of air was displaced by distillate, and second, trapped air has been found to dissolve rapidly in the distillate at high pressure. Experimental evidence will be given to confirm the belief that any errors in compressibility arising from trapped air are negligible.

Penetration of distillate into the small voids in these experiments was accompanied by a rapid decrease in pressure with time. This effect occurred only when the specimen was initially subjected to high pressures and was absent on subsequent compressions. The rate of penetration was not measured but was observed to decrease with time and, although considerable time was allowed to attain equilibrium at the maximum pressure, it was most probable that slow penetration occurred during the initial measurement in each experiment.

Penetration of distillate into the specimens produced an apparent decrease in the quantity of liquid in the pressure vessel. The disappearance of liquid effectively increased the required displacement of the piston, so that in most instances the maximum stroke was exceeded before reaching 10,000 atm. Generally, more distillate was added to permit attainment of 10,000 atm, but in some instances measurements were made only to the maximum pressure attainable on the initial compression. In most of the latter instances the maximum was 9,000 atm, but in one instance it was only 8,000 atm.

The experimental error in these data is subject to some uncertainty. In general, with the techniques used here it has been concluded that the data may be reproduced to within ± 0.0004 in $-\Delta V/V_0$ [9]. Such precision is readily obtained when the correction terms [6] are kept reasonably small. In the present studies the correction terms were frequently undesirably large and were in general not subject to control because of the penetration of distillate into the specimen and variations in the real volume of the specimens. The actual volume of the specimen studied was likewise subject to some uncertainty arising from occasional loss of small fragments in handling prior to weighing hydrostatically.

Although this compilation of known sources of error is long, most of the errors involved are quite small and in many instances may mutually compensate. It is believed that each measured value of compression in these studies may be considered reliable to within ± 0.0008 . The differences between data obtained with duplicate specimens may be somewhat greater than this and represent differences in the specimens themselves. Therefore, some of the conclusions based on small differences between different specimens are subject to some uncertainty.

3.2. Compression of Dried Cement Pastes of Different Ages and Water-Cement Ratios

Measurements were made on dry cement A before mixing it with water and after hydration for various periods of time. These specimens were prepared

with nominal water-cement ratios 0.3, 0.5, and 0.7 to determine whether the distillate penetrated all the voids or whether a portion of the change in volume was due to compression of voids. The data on these specimens, which were all dried in a vacuum for 1 week, are given in tables 2 to 5.

All compressions as tabulated are based on the reference pressure of 2,000 atm, but may be calculated from 1 atm by adding to each value of the corresponding column the (positive) compression given at 1 atm. At the head of each column the nominal water-cement ratios are given. The actual water content was probably somewhat less than that indicated by the ratios given, which, however, serve to designate specimens differing significantly in total void content. Below each water-cement ratio are given in order the nonevaporable-water content based on the weight of the original cement, the density of the specimen, and the volume of the specimen at 1 atm.

TABLE 2. Compression of hardened cement A paste cured for 1 week

Nominal water-cement ratio	0.3	0.5		0.7
Nonevaporable water content, % of original cement	12.1	11.1	11.1	10.8
Density at 21° C, g/cm ³	2.679	2.706	2.711	2.712
Volume of test specimen, cm ³	8.361	5.869	5.702	4.737
Pressure	Compression, $-\Delta V/V_0$			
10,000	0.0193	0.0193	0.0176	0.0181
9,000	.0178	.0176	.0155	.0176
8,000	.0161	.0157	.0135	.0162
7,000	.0136	.0127	.0119	.0136
6,000	.0114	.0106	.0095	.0112
5,000	.0090	.0080	.0074	.0090
4,000	.0062	.0051	.0048	.0060
3,000	.0031	.0020	.0020	.0030
2,000	.0000	.0000	.0000	.0000
1,000	-----	-----	-.0016	-----
1	-.006	-.005	-.005	-.006

TABLE 3. Compression of hardened cement A paste cured for 1 month

Nominal water-cement ratio	0.3	0.5	0.7
Nonevaporable water content, % of original cement	15.2	16.0	15.4
Density at 21° C, g/cm ³	2.559	2.567	2.584
Volume of test specimen, cm ³	8.951	6.550	5.211
Pressure	Compression, $-\Delta V/V_0$		
10,000	0.0255	0.0233	0.0217
9,000	.0211	.0214	.0199
8,000	.0195	.0185	.0175
7,000	.0169	.0155	.0148
6,000	.0136	.0129	.0125
5,000	.0107	.0097	.0089
4,000	.0077	.0064	.0061
3,000	.0036	.0025	.0050
2,000	.0000	.0000	.0000
1	-.008	-.006	-.006

TABLE 4. Compression of hardened cement A paste cured for 6 months

Nominal water-cement ratio	0.3	0.5	0.7
Nonevaporable water content, % of original cement	16.7	20.1	32.8
Density at 21° C, g/cm ³	2.557	2.456	2.333
Volume of test specimen, cm ³	8.879	7.111	6.338
Pressure	Compression, $-\Delta V/V_0$		
<i>atm</i>			
10,000	0.0205	0.0224	0.0276
9,000	.0186	.0214	.0269
8,000	.0168	.0192	.0246
7,000	.0155	.0168	.0217
6,000	.0109	.0141	.0184
5,000	.0083	.0115	.0158
4,000	.0053	.0085	.0119
3,000	.0010	.0038	.0060
2,000	.0000	.0000	.0000
1	-.006	-.008	-.01

TABLE 5. Compression of unhydrated cement A powder

Density at 21° C, g/cm ³	3.081 ^a
Volume of test specimen, cm ³	7.687
Pressure	Compression, $-\Delta V/V_0$
<i>atm</i>	
10,000	0.0166
9,000	.0150
8,000	.0130
7,000	.0113
6,000	.0089
5,000	.0078
4,000	.0063
3,000	.0034
2,000	.0000
1,000	-.0032
1	-.006

^a Density by ASTM method C188-44 is 3.18 g/cm³.

In table 2, measurements are given for two specimens of water-cement ratio 0.5. The differences noted in data on these duplicates, particularly at the higher pressures, are believed to be larger than the experimental errors involved and, therefore, are indicative of differences in the specimens themselves.

The data in table 2 indicate very little difference in the compressions of cement pastes of different water-cement ratio after 1 week of curing. This strengthens the argument that the values obtained represent compression of the hydrated cement and do not reflect the compression of voids, except possibly submicroscopic pores believed to be present in all pastes regardless of the water-cement ratios. The differences in porosity of the specimens were quite evident from their behavior on initial compression. Time effects attributed to penetration of distillate into voids were observed, which were roughly proportional to the water-cement ratio, being extremely large in the specimens with a ratio of 0.7 and practically nonexistent in specimens with ratio 0.3.

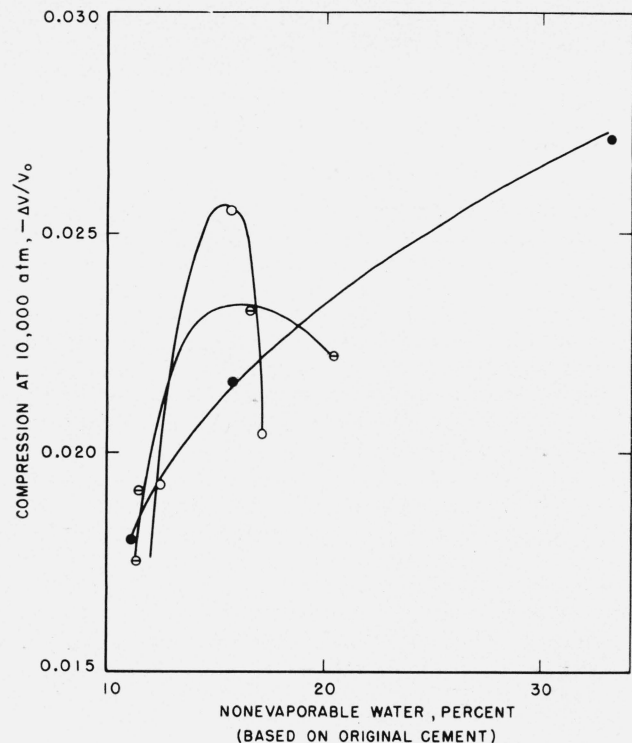


FIGURE 1. Effect of nonevaporable-water content and water-cement ratio on compression.

○, Water-cement ratio 0.3; □, water-cement ratio 0.5; ●, water-cement ratio 0.7.

On comparing the compressions for the different curing periods shown in tables 2, 3, and 4, interesting differences may be noted. The data indicate that the compression initially increases with increased curing and then may reach a maximum and decrease with further curing, with the time of cure required to reach a maximum being dependent on the water-cement ratio. This behavior is illustrated in figure 1, where the compression at 10,000 atm is plotted against the nonevaporable water content. It will be noted that a well-defined maximum is shown for the lowest water-cement ratio; a similar maximum is absent in the highest water-cement ratio, whereas the intermediate water-cement ratio shows an intermediate behavior. It must be noted that the effects of curing period and water content shown in figure 1 are subject to some uncertainty caused by specimen-to-specimen variability. With these reservations in mind, however, the results suggest that the gel structure laid down in the first few weeks of hydration is being reinforced during subsequent hydration. This process is more marked at lower water-cement ratios, because there is not only less water but there is also less space for deposition of new gel [11]. At low water-cement ratio the rate of hydration is also slower in the later stages than in specimens of higher water-cement ratio. Possibly the maximum might be observed at all water-cement ratios if hydration were continued long enough.

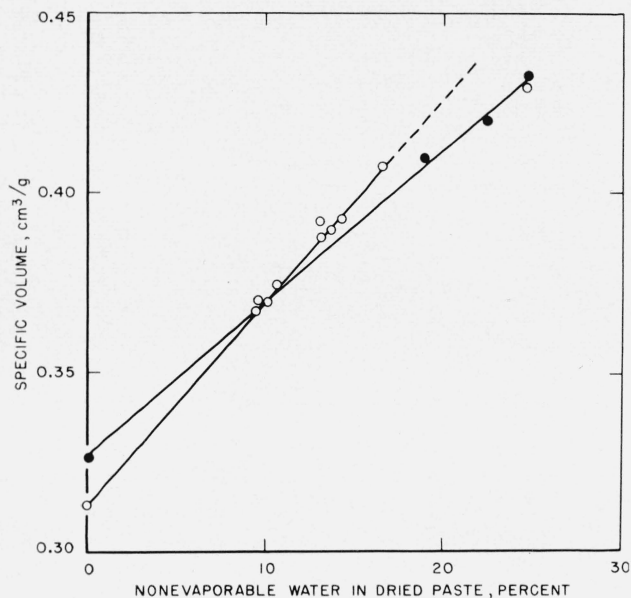


FIGURE 2. Effect of nonevaporable-water content on specific volume of hydrated portland and aluminous cements.

○, Portland cement; ●, aluminous cement.

The compression of the parent unhydrated cement is given in the data of table 5. This material was investigated as a powder and was studied in the steel cylinder as described previously. Although this material was investigated as a powder, the data are considered comparable with data obtained with cast cylinders. Evidence for the validity of this conclusion has been obtained in experiments comparing compressions of powdered and molded specimens of organic polymers [10].

Useful by-products of the compressibility measurements are density determinations on specimens that have been evacuated and then impregnated with distillate at a pressure of 10,000 atm. The values so obtained should represent a rather uniform penetration of the pore structure by the distillate. Powers and Brownyard [11] have expressed the volume of the solid phase in hydrated cement as the volumes of the original cement and the nonevaporable water according to the relationship

$$V_s = cv_c + w_n v_n, \quad (3)$$

where V_s is the volume of the solid phase, c the weight of the original cement, v_c the specific volume of the original cement, w_n the weight of nonevaporable water, and v_n the hypothetical specific volume of the nonevaporable water. In terms of specific volume of the solid phase, an equivalent relationship may be written as

$$v_s = x_c v_c + y_n v_n, \quad (4)$$

where, in addition to terms previously defined, v_s is the specific volume of the solid phase, and x_c and y_n are the weight fractions of cement and

nonevaporable water, respectively. With the necessary relationship

$$x_c = 1 - y_n \quad (5)$$

eq (4) may be transformed into

$$v_s = v_c + (v_n - v_c)y_n. \quad (6)$$

From this equation a plot of y_n against v_s should yield a straight line of slope $(v_n - v_c)$ and intercept v_c on the v_s axis. Values of y_n the fraction of nonevaporable water in the dried specimen (expressed as percent), and v_s are plotted in figure 2. A linear relationship is obtained which by extrapolation gives the specific volume of unhydrated cement at zero water content. The experimental value for unhydrated cement in figure 2 was obtained with a Le Chatelier flask (ASTM standard method C188-44), because the value obtained after compression appeared to be high and an error in weighing was suspected. The nonevaporable water content of the portland cement specimen with the highest specific volume in figure 2 is also suspected to be in error, because it is greater than values for specimens prepared from the same cement and cured a year. Such an error might easily occur through the loss of a fragment of specimen which would be calculated as a loss of water. The nonevaporable water content of this specimen is given in table 4 as 32.8 percent of the weight of the original cement and is also plotted in figure 1. Powers and Brownyard give 20 to 25 percent, based on the weight of the cement, as a reasonable estimate for the nonevaporable water content of a specimen close to ultimate hydration [13]. The linearity observed below about 20-percent nonevaporable water in figure 2 offers strong evidence that the distillate penetrated the same domains of the structure irrespective of age or water-cement ratio. The exact dimensions of the finest pores in cement gel are somewhat conjectural but may be of the order of a few angstrom units in diameter [13,14]. It is doubtful if distillate penetrated all these ultrafine pores. However, penetration undoubtedly occurred in all pores whose size or number could be varied by changing the water-cement ratio.

From the slope of the line of figure 2 and the value of v_c , a value for the hypothetical specific volume of the nonevaporable water, v_n , was calculated. The value obtained was 0.87 ml/g. This value is higher than the 0.82 ml/g reported by Powers and Brownyard from measurements of density of a number of cements by helium displacement [11] or the value of 0.74 ml/g obtained by Copeland [12], using water as a displacement medium. This indicates that distillate did not penetrate the structure to the same extent as did helium or water. Another factor contributing to this difference may be the difference in the method of drying. These specimens were dried as ½- by 4-in. cylinders, whereas the specimens of Powers and Brownyard [11,15] and Copeland [8,12] were dried in granular form. Somewhat more water may be removed in the latter form.

3.3. Effect of Evaporable Water on Compression of Hydrated Cement

The effect of evaporable-water content on the compression of cement of a given age and water-cement ratio was most interesting. In these experiments six specimens of cement A mixed with a water-cement ratio of 0.5 were cured for 1 week. Following the curing period the specimens were dried in a vacuum for periods varying from 15 min to 1 week before the testing. The specimen dried for 1 week retained 10.9 percent of water, based on the weight of the cement used in preparing the specimen. Although more rigorous drying procedures might have removed a portion of this water, the 10.9 percent of water was arbitrarily taken to represent the nonevaporable-water content of all the specimens. The compression data obtained on these specimens are given in table 6, and the compression-pressure behavior is shown graphically in figure 3. In figure 3 the compressions of the specimens with evaporable-water contents of 2.2 and 5.2 percent were only slightly greater than the driest specimen. The specimens with evaporable-water contents of 17.5 percent or more, however, were highly compressible and the compression increased markedly with increasing water content. Although the increased compression extends over the whole pressure range, it will be noted in the three specimens of high moisture content that the curves are nearly parallel above about 5,000 atm.

TABLE 6. Effect of evaporable water on compression of hardened cement A paste (1-week cure)

Evaporable-water content, % of original cement.....	32.4	26.9	17.5	5.2	2.2	0
Density, g/cm ³	1.951	2.100	2.270	2.580	2.650	2.735
Volume of test specimen, cm ³	10.508	8.849	7.874	6.316	5.897	7.709
Pressure	Compression, $-\Delta V/V_0$					
atm	0.324	0.269	0.175	0.052	0.022	0.000
10,000	0.0777	---	---	0.0219	0.0225	0.0182
9,000	.0733	0.0669	0.0465	.0198	.0204	.0172
8,000	.0690	.0628	.0426	.0178	.0182	.0151
7,000	.0641	.0579	.0375	.0148	.0153	.0126
6,000	.0589	.0524	.0323	.0122	.0127	.0102
5,000	.0528	.0442	.0272	.0095	.0100	.0074
4,000	.0445	.0376	.0216	.0064	.0068	.0048
3,000	.0326	.0253	.0130	.0025	.0029	.0017
2,000	.0000	.0000	.0000	.0000	.0000	.0000
1,000	-.0168	-.0120	-.0127	---	---	---
1	-.03	-.02	-.02	-.006	-.006	-.005

Compressibility—the slope of the curves—is less affected by moisture content above 5,000 atm even at high evaporable-water content. Below about 4,000 atm a rapid change in compression is observed at the higher moisture contents, and the compression in this region of pressures is a strong function of the water content. Below 4,000 atm the sigmoid shape of the compression curve clearly indicates that a transition is occurring. The transition is not sharp and appears to occur principally between 2,000 and 3,000 atm. Large thermal effects are associated

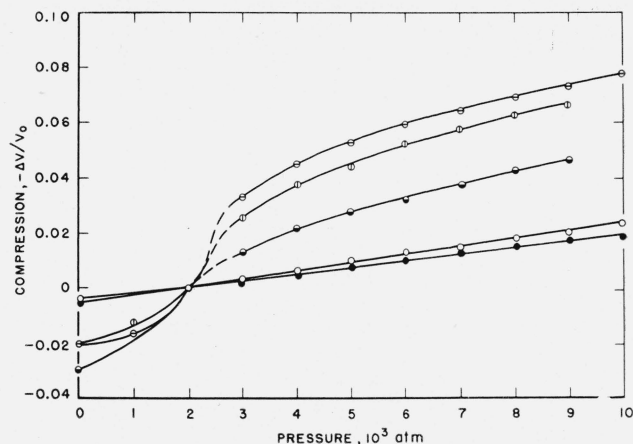


FIGURE 3. Effect of evaporable-water content on the compression of hydrated portland cement A, type I.

○, 32.4 percent of evaporable water; ⊕, 26.9 percent of evaporable water; ●, 17.5 percent of evaporable water; ○, 2.2 and 5.2 percent of evaporable water; ●, 0 percent of evaporable water.

with this transition and these are readily observed experimentally [9] in their effect on the pressure. From the experimental observations of the thermal effects it is concluded that the transition is not occurring below 2,000 atm but that it persists to pressures as high as 4,000 atm. No experimental evidence was found for any comparable discontinuity at the lower moisture contents, and it is concluded that the phenomenon requires moisture.

The transition is completely analogous to a phase transition produced isobarically by changing the temperature, i. e., freezing point. The fact that this transition occurs over a rather wide pressure interval is understandable because in a complex material such as cement many other substances may enter into the phase change. In this respect it is analogous to the freezing of an impure material.

A different picture of the process may be obtained by considering the compression isobarically in relation to the evaporable water content. Isobars at a few representative pressures are given in figure 4. The broken lines in figure 4 represent compressions calculated for ideal mixtures of water and dry paste and converge on the compression axis with the corresponding experimental isobars. The calculated compressions were based on the known compression of water [16] and dry paste (the specimen containing no evaporable water in table 6) and their respective volume fractions. Significant divergence of the calculated and experimental curves appears at pressures of 3,000 atm and higher and approximately 10 percent or more evaporable moisture. At 1,000 atm the calculated and measured data are in substantial agreement over the whole moisture range. It will also be noted that divergence of calculated and measured values increases rapidly with increasing moisture content but is relatively insensitive to changing pressure at a given moisture content at the higher pressures. These observations are consistent with the behavior to be expected from a transition centered between 2,000 and 3,000 atm.

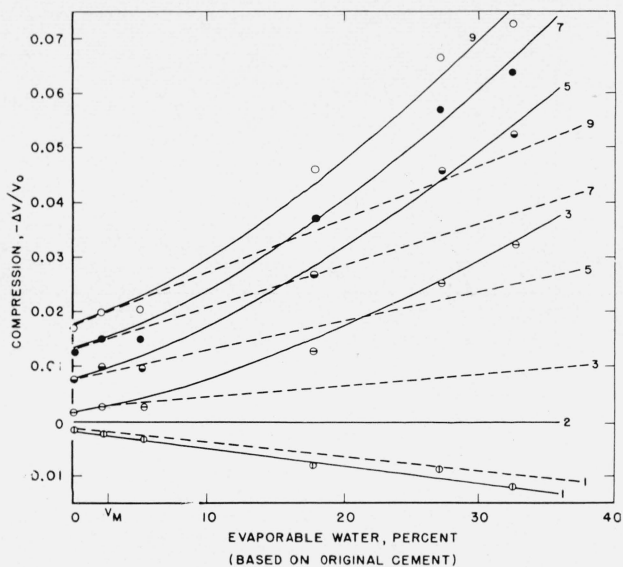


FIGURE 4. Calculated and measured isobars for portland cement as functions of evaporable-water content.

Digits at right of each isobar denote the presence in kilokatmospheres. — — — —, Measured; — — — —, calculated.

Water-vapor sorption measurements have been made on separate specimens of hardened paste prepared from the same cement and cured 1 week over water. If the adsorption of water vapor by hydrated cement is a multilayer adsorption process, in the range of relative humidity over which the Brunauer-Emmett-Teller (BET) equation applies, V_m is the amount of water theoretically required to cover the total surface of the hydrated cement with a layer of water 1 molecule thick. A V_m value of 2.8 percent of evaporable water was calculated from such data by the BET equation [17]. From figure 4 it is noted that the correlation between the experimental and calculated compressions deviates appreciably above an evaporable water content 2 or 3 times V_m .

The data at low moisture contents are of interest in connection with questions concerning the nature of this water. Within the experimental errors no essential differences exist between calculated and measured compressions at low moisture contents as shown in figure 4. Although the experimental points at 5.2 percent of evaporable water are indicated as lying somewhat below the calculated curves, there is some doubt as to whether this is of real significance. However, all data shown in figure 4 are based on evaporable-water content, and all specimens are considered to contain 10.9 percent of nonevaporable water. The compression curve for the specimen containing 10.9 percent water has been compared with a similar curve for unhydrated cement and also with a curve calculated for a mixture of unhydrated cement and 10.9 percent of water, assuming the specific volume of nonevaporable water to be 0.87 ml/g. These results are shown in figure 5. Similar curves could be made from the data in tables 2 to 5. Although all the compression curves would

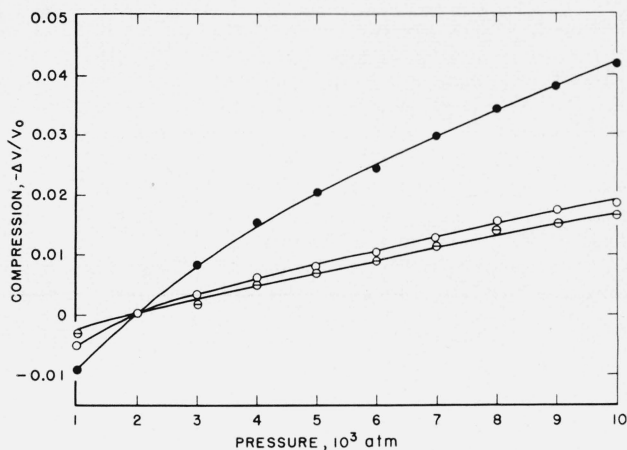


FIGURE 5. Calculated and measured compressions for portland cement as affected by nonevaporable-water content.

●, Calculated (unhydrated cement and mixture of 10.9 percent of liquid water); ○, measured (hydrated cement with 10.9 percent of nonevaporable water); ⊖, measured (unhydrated cement).

not coincide as closely with the unhydrated cement as the specimen shown in figure 5, all results would show that the experimental compressions were much less than those calculated for corresponding mixtures of unhydrated cement and water. Thus compressibility measurements confirm what would seem evident from other considerations, namely, that nonevaporable water is accommodated differently in the structure of hydrated cement than evaporable water.

Before describing the experiments that were conducted to ascertain the source of the transition observed in hydrated portland cement containing large amounts of evaporable water, it is of interest to consider certain possible explanations for the phenomenon. Water is known to freeze to ice VI at approximately 8,700 atm at room temperature [18]. Liquid water in cement will exist in a solution which will be expected to freeze at still higher pressures. A marked reduction of this freezing point by some 6,000 atm is not expected. It has been proposed, however, that adsorbed moisture and water present in fine capillaries are subject to extreme surface forces and, therefore, normally exist under high hydrostatic pressure [19]. Such concepts have frequently been advanced in connection with theories of bound water which will not be reviewed here. A small increase in external hydrostatic pressure on such tightly bound water might exceed the freezing pressure and produce the transition observed here. However, such an explanation should lead to observations of a transition even at low moisture contents at which it appears to be completely absent. In addition, no similar effects were observed in studies on fibrous polymers containing as much as 30 percent of moisture [20]. It has been suggested, also, that the high hydrostatic pressure might rupture small particles of cement as a result of nonhydrostatic forces at grain boundaries, thereby producing an apparent transition. However, all data reported here were obtained on decreasing pressure and in these studies measurements may be made only

in this direction because of penetration of distillate into the voids upon compression. However, additional observations indicated that the transition was completely reversible, and it is difficult to conceive of a reversible but destructive physical phenomenon. Furthermore, as later data will show, a cement with no detectable transition has been studied. This fact alone essentially eliminates the forementioned explanations for the transition.

From the data already presented it appears that some hydrated material in cement produced the observed transition. The wide pressure range of the transition is attributed to the fact that hydrated cement is not a pure substance.

3.4. Source of the Transition in Hydrated Cement Containing Large Amounts of Evaporable Water

A number of experiments were performed to study the transition in detail and to ascertain the material responsible for the phenomenon. In order to determine whether the transition disappeared permanently once the sample was dried, or whether it could be regenerated by rewetting, the following experiment was performed with three specimens prepared from cement A, nominal water-cement ratio 0.5, cured 1 week. The first specimen was tested immediately following the 1-week cure, with most of its evaporable water intact. The other two specimens were dried in vacuum for 1 week and one was tested in the dried condition. The last specimen was rewet in liquid water and tested immediately. The results obtained in these experiments are shown graphically in figure 6. It is apparent that the transition appearing in the original specimen is eliminated by drying and regenerated on rewetting the dried specimen. Whatever the source of the transition, it must arise from a material formed rapidly in the presence of water.

Compressibility measurements were made on hardened aluminous-cement pastes containing different amounts of evaporable water. This was done with the idea that some structural similarity might exist between the hydrated tricalcium aluminate of portland cement and some of the hydrated compounds in aluminous cement paste [21]. No transition was observed with hydrated aluminous cement containing large amounts of evaporable water. These data will be discussed in the next section.

Compression measurements made on silica gel containing a large amount of evaporable water showed no transition within the pressure range investigated. A specially prepared cement containing no gypsum was hydrated and observed to exhibit a small transition on compression. These data, together with those on the silica gel, are only qualitative and are not given in tabular form. The graphical data, however, are shown in figure 7. It is concluded that neither gypsum nor calcium sulfoaluminates were involved in the transition.

Further studies were made using a specimen of tricalcium silicate mixed with approximately an equal weight of water and cured for 1 week. Analy-

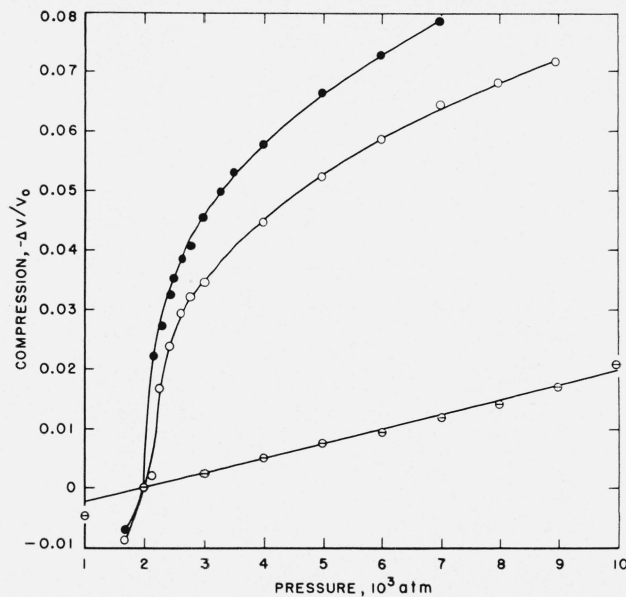


FIGURE 6. Effect of drying and rewetting on the transition in hydrated portland cement.

○, Original moisture content; ⊖, dried in a vacuum, ●, dried in a vacuum and rewet.

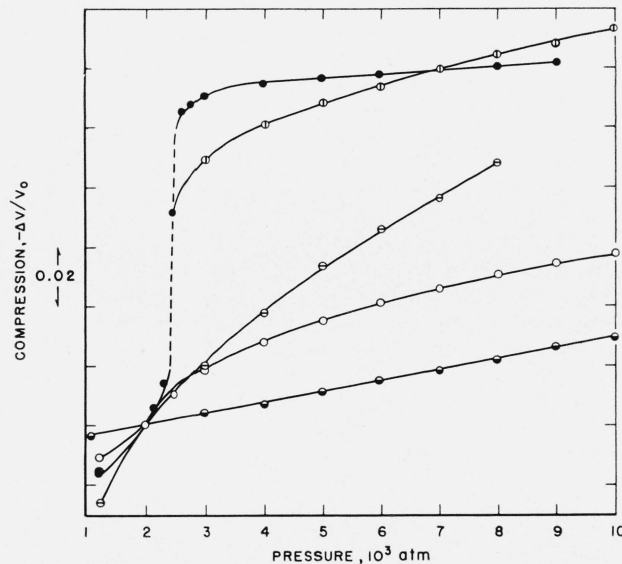


FIGURE 7. Comparison of compressions of various materials.

○, Hydrated tricalcium silicate containing evaporable water; □, hydrated gypsum-free cement containing evaporable water; ●, Ca(OH)_2 (containing water); ⊖, Ca(OH)_2 (dry); ⊖, silica gel (containing water).

sis of part of the specimen showed that it contained 9.9 percent of nonevaporable water, expressed as percentage of the tricalcium silicate. The compression data showed a very strong transition between 2,000 and 3,000 atm, as shown in figure 7. The transition here is much sharper than observed in the cements, but occurs in the same pressure interval. On drying and remeasuring the test specimen, the transition disappeared as in the hydrated cements.

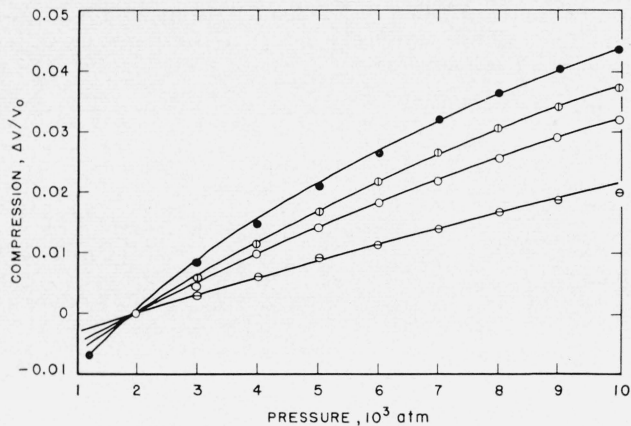


FIGURE 8. Effect of evaporable water on compression of hydrated aluminous cement.

●, 21.2 percent of evaporable water; ○, 18.1 percent of evaporable water; □, 15.8 percent of evaporable water; ○, 0 percent of evaporable water.

As free $\text{Ca}(\text{OH})_2$ is one of the hydration products of tricalcium silicate and other cement compounds [22], a final experiment was performed on $\text{Ca}(\text{OH})_2$ in the wet and dry states. A very strong transition was observed in the wet lime, which was completely absent in the dried material. The graphical data on wet $\text{Ca}(\text{OH})_2$ are given in figure 7. It will be noted that the transition in this material occurs at approximately the same pressure and is noticeably sharper than that in the tricalcium silicate.

Although the transition in wet cement is extended over a pressure interval, the major portion of the volume change occurs at essentially the same pressure at which the transition takes place in wet $\text{Ca}(\text{OH})_2$. The chance of finding two different materials having similar transition temperatures at 1 atm is quite small. The chance of finding different materials having the same transition pressure at a given temperature is remote because pressure-induced transitions are less common than those of thermal origin. It may be concluded, therefore, that the discontinuity in volume observed in hydrated cement containing appreciable evaporable water arises from wet $\text{Ca}(\text{OH})_2$, which is liberated in the hydration of portland cement. The system $\text{Ca}(\text{OH})_2\text{-H}_2\text{O}$ has been investigated under pressure in additional experiments reported elsewhere, and it has been concluded that the transition arises from the formation of a hydrate of $\text{Ca}(\text{OH})_2$ [23].

3.5. Aluminous Cement

The aluminous cements occur in a different region of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system from portland cements [22]. The compounds $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, $\text{CaO}\cdot 3\text{Al}_2\text{O}_3$, and $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$ are believed to constitute the major portion of aluminous cements instead of the compounds $2\text{CaO}\cdot \text{SiO}_2$, $3\text{CaO}\cdot \text{SiO}_2$, $3\text{CaO}\cdot \text{Al}_2\text{O}_3$, and $4\text{CaO}\cdot \text{Al}_2\text{O}_3\cdot \text{Fe}_2\text{O}_3$, which are believed to exist in portland cements [22, 24]. Aluminous cements hydrate more rapidly than portland cements, with a corresponding more rapid evolution of heat. Free

lime is not one of the final end products of hydration in the aluminous cements, as in portland cement [25].

Studies made on aluminous cement included the effects of evaporable water and length of cure. Compression data on these specimens are given in tables 7 and 8 and are shown in part in figure 8. The specimen of highest evaporable water content in table 7 received no drying treatment; the driest specimen was dried in vacuum for 1 week, and had a nonevaporable-water content of 29.2 percent. In figure 8 it is observed that the compression increases with evaporable-water content, but from observations during the measurements it was evident that there was no transition similar to that observed in the portland cements. In general, it was found that the compressibility of the hydrated aluminous cement was somewhat higher than that of the hydrated portland cement, but part of this difference may arise from a somewhat higher nonevaporable-water content in the aluminous-cement pastes.

TABLE 7. Effect of evaporable-water content on compression of hardened aluminous-cement paste cured for 1 week

Evaporable-water content, % of original cement	21.2	18.1	15.8	0.0
Density, g/cm^3	2.092	2.131	2.173	2.390
Volume of test specimen, cm^3	9.894	9.642	9.180	7.327
Pressure	Compression, $-\Delta V/V_0$			
atm				
10,000	0.0436	0.0373	0.0319	0.0202
9,000	.0402	.0340	.0290	.0186
8,000	.0364	.0307	.0257	.0167
7,000	.0321	.0267	.0220	.0142
6,000	.0267	.0218	.0182	.0116
5,000	.0211	.0168	.0142	.0091
4,000	.0148	.0113	.0102	.0061
3,000	.0086	.0052	.0057	.0032
2,000	.0000	.0000	.0000	.0000
1,220	-.0068	-----	-.0064	-----
1	-.014	-.012	-.01	-.006

TABLE 8. Compression of hardened aluminous-cement paste

Cure	1 day	1 month	7½ month
Nonevaporable - water content, % of original cement	23.7	33.2	37.5
Density at 21° C, g/cm^3	2.446	2.318	2.263
Volume of test specimen, cm^3	7.027	7.708	8.348
Pressure	Compression, $-\Delta V/V_0$		
atm			
10,000	0.0136	0.0385	0.0298
9,000	.0122	.0350	.0284
8,000	.0102	.0317	.0254
7,000	.0084	.0281	.0220
6,000	.0065	.0246	.0182
5,000	.0047	.0200	.0138
4,000	.0028	.0156	.0094
3,000	.0018	.0088	.0042
2,000	.0000	.0000	.0000
1,000	-.0017	-----	-.0052
1	-.003	-.015	-.009

The measured specific volumes of the specimens of aluminous-cement pastes have been plotted in accordance with eq (6). The value for the unhydrated cement was obtained with the Le Chatelier flask because no compression measurements were made on this material. The graph of these data is shown in figure 2 and again indicates a linear relationship. The slope of the line, which is somewhat less than that found for portland cement, yields a value of 0.75 ml/g for the hypothetical specific volume of the nonevaporable water as compared to the 0.87 ml/g found for portland cement by the same method. This difference suggests that on hydration the system, aluminous cement plus water, undergoes a greater contraction than portland cement. Lea and Desch [22] have cited the work of Le Chatelier [26] and Gessner [27] in support of a similar conclusion.

A graph of the isobars of aluminous cement similar to figure 4 for the portland cement is not included because the number of specimens was limited. However, experimental compression values were lower than values computed on the assumption that the compressions of dried paste and evaporable water were additive. This is quite different from moist portland-cement paste and adds support to the view that hydrated aluminous cement undergoes no transition like that produced in hydrated portland cement, or if any such transition occurs while the paste is under pressure, it is greatly reduced in extent.

According to the data in table 8 the compression increases with hydration up to 1 month, but it is less than the maximum at 7½ months. In other words, aluminous cement also shows a maximum similar to the ones shown in figure 1. The initial increase in compression is considerably greater than was found in the portland cement, but at least a portion of the effect may arise from the greater nonevaporable-water content in aluminous cement.

3.6. Compression of Different Types of Portland Cement

In these studies measurements were made on hydrated cements of different types mixed with a water-cement ratio of 0.5. Results obtained with specimens cured 1 week and vacuum dried 1 week are given in table 9. Measurements on specimens cured 1 month and longer are given in tables 10 and 11. These cements showed differences in rate of hydration, as evidenced by their different moisture contents after drying. However, the correlation between degree of hydration and compression was only fair, which suggests other factors also play a part in determining the behavior of hydrated cement under pressure. Hydrated type II cement was consistently a little less compressible than the others.

The compressions of only the types II and V cements were measured at three ages so that plots similar to the ones shown in figure 1 could be made. Such plots are not given for these specimens, but it

is evident that the type V cement had a maximum similar to those shown in figure 1, and the type II merely showed curvature.

TABLE 9. Compression of hardened pastes of various types of cements (1-week cure)

Type of cement..... Nonevaporable water content, % of original cement..... Density at 21° C, g/cm ³ Volume of test specimen, cm ³	I	II	III	IV	V
	15.0	11.9	17.5	12.0	10.8
	2.597	2.683	2.524	2.697	2.705
	6.422	5.745	6.538	6.271	5.936
Pressure	Compression, $-\Delta V/V_0$				
<i>atm</i>					
10,000	0.0189	-----	0.0211	0.0170	0.0170
9,000	.0177	0.0121	.0192	.0160	.0160
8,000	.0155	.0107	.0167	.0139	.0139
7,000	.0136	.0091	.0144	.0119	.0119
6,000	.0111	.0077	.0118	.0095	.0099
5,000	.0086	.0052	.0088	.0072	.0074
4,000	.0054	.0035	.0059	.0044	.0047
3,000	.0033	.0012	.0030	.0031	.0024
2,000	.0000	.0000	.0000	.0000	.0000
1,260	-----	-.0018	-.0032	-.0025	-.0020
1	-.006	-.005	-.006	-.005	-.005

TABLE 10. Compression of hardened pastes of various types of cements (1-month cure)

Type of cement..... Nonevaporable water content, % of original cement..... Density at 21° C, g/cm ³ Volume of test specimen, cm ³	II	IV	V
	16.9	18.2	12.8
	2.518	2.525	2.657
	6.769	6.829	6.354
Pressure	Compression, $-\Delta V/V_0$		
<i>atm</i>			
10,000	-----	0.0207	0.0232
9,000	-----	.0194	.0196
8,000	0.0151	.0173	.0170
7,000	.0131	.0149	.0145
6,000	.0105	.0124	.0118
5,000	.0091	.0097	.0091
4,000	.0057	.0069	.0059
3,000	.0029	.0036	.0029
2,000	.0000	.0000	.0000
1	-.006	-.007	-.006

TABLE 11. Compression of hardened pastes of various types of cements (7½-month cure)

Type of cement..... Nonevaporable water content, % of original cement..... Density at 21° C, g/cm ³ Volume of test specimen, cm ³	I	II	V
	25.9	21.7	20.0
	2.367	2.433	2.481
	7.687	7.373	6.782
Pressure	Compression, $-\Delta V/V_0$		
<i>atm</i>			
10,000	0.0237	0.0177	0.0190
9,000	.0220	.0175	.0186
8,000	.0203	.0161	.0166
7,000	.0176	.0144	.0144
6,000	.0146	.0120	.0124
5,000	.0114	.0089	.0096
4,000	.0080	.0057	.0069
3,000	.0046	.0029	.0038
2,000	.0000	.0000	.0000
1,000	-.0048	-.0039	-.0017
1	-.008	-.006	-.006

3.7. Compressibility and Elastic Constants of Cement

The coefficient of compressibility, β , is defined by means of the relationship

$$\beta = -dV/V_0 dP, \quad (7)$$

where V_0 is the volume at 1 atm and dV/dP the infinitesimal change in volume divided by the infinitesimal change in pressure. Values of β can be obtained as the slopes of the $-\Delta V/V_0$ versus P curves shown. For most of the dried cements β decreases with increasing pressure only slightly and, therefore, average compressibilities above and below 5,000 atm have been calculated from the equation

$$\beta = -\Delta V/V_0 \Delta P, \quad (8)$$

where ΔV represents the change in volume between the maximum or minimum pressure and 5,000 atm,

TABLE 12. Average compressibility of hydrated cements after vacuum drying for 1 week

Curing period	Average compressibility, $10^{-6}/\text{atm}$	
	1 to 5,000 atm	5,000 to 10,000 atm
Cement A: Water-cement ratio 0.3		
1-week	3.0	2.1
1-month	3.7	3.0
6-month	2.9	2.6
Cement A: Water-cement ratio 0.5		
1-week	2.6	2.2
1-month	3.1	2.7
6-month	3.9	2.2
Cement A: Water-cement ratio 0.7		
1-week	3.0	1.8
1-month	3.0	2.5
6-month	5.2	2.4
Type I cement: Water-cement ratio 0.5		
1-week	2.9	2.1
7½-month	3.9	2.5
Type II cement: Water-cement ratio 0.5		
1-week	2.0	1.8
1-month	3.0	2.0
7½-month	3.0	1.8
Type III cement: Water-cement ratio 0.5		
1-week	3.0	2.0
Type IV cement: Water-cement ratio 0.5		
1-week	2.4	2.0
1-month	3.1	2.2
Type V cement: Water-cement ratio 0.5		
1-week	2.5	1.9
1-month	3.0	2.8
7½-month	3.1	1.9

and ΔP the corresponding change in pressure. Average compressibilities calculated from eq (8) are given for a number of cements in tables 12 to 14.

Table 12 contains data for dried specimens and shows the decrease in average compressibility with increasing pressure. Average compressibilities below 5,000 atm show a maximum with increasing curing time only for hydrated cement A, of water-cement ratio 0.3, whereas the corresponding data above 5,000 atm exhibit the maximum for all water-cement ratios for which the comparison could be made. Table 13 contains corresponding data for specimens of various evaporable-water contents. The marked difference in compressibilities noted above and below 5,000 atm at the higher moisture contents is directly attributable to the transition occurring in these specimens. Where such a disparity in compressibility is effected by pressure changes of this order of magnitude, it is most probable that a transition of some sort is involved. In such cases no real significance is attached to the compressibility, which is averaged over the pressure interval containing the transition. In table 14 corresponding data are given for the aluminous cements.

On averaging the data for the dry hydrated portland cement specimens of tables 12 and 13 regardless of age, water-cement ratio, or type of cement, an average compressibility of $3.1 \times 10^{-6} \text{ atm}^{-1}$ is obtained below 5,000 atm and the corresponding value above 5,000 atm is $2.2 \times 10^{-6} \text{ atm}^{-1}$. The standard deviations of these figures are $0.7 \times$

TABLE 13. Average compressibility of hydrated cement A containing different amounts of evaporable water

(water-cement ratio 0.5; 1-week cure)

Evaporable water	Compressibility, $10^{-6}/\text{atm}$	
	1 to 5,000 atm	5,000 to 10,000 atm
<i>Percent</i>		
32.4	14.6	5.0
26.9	12.8	5.7
17.5	9.4	4.8
5.2	3.1	2.5
2.2	3.2	2.5
0	2.5	2.2

TABLE 14. Average compressibility of hydrated aluminous cement of different age and evaporable-water content

(Water-cement ratio 0.5)

Curing period	Evaporable water	Compressibility, $10^{-6}/\text{atm}$	
		1 to 5,000 atm	5,000 to 10,000 atm
	<i>Percent</i>		
1 day	0	1.5	1.8
1 week	21.2	7.0	4.5
Do	18.1	5.8	4.1
Do	15.8	4.8	3.5
Do	0	3.0	2.2
1 month	0	7.0	3.7
7½ months	0	4.6	3.2

10^{-6} atm⁻¹ and 0.3×10^{-6} atm⁻¹, respectively. The single specimen of unhydrated cement powder had a compressibility of 2.8×10^{-6} atm⁻¹ below 5,000 atm and 1.6×10^{-6} atm⁻¹ above 5,000 atm.

From the average compressibility and one other elastic constant, the elastic moduli may be calculated from the well-known relationships [5]

$$E = 3(1 - 2\nu)/\beta \quad (9)$$

$$G = 3(1 - 2\nu)/2\beta(1 + \nu), \quad (10)$$

where E is Young's modulus, ν Poisson's ratio, and G the shear modulus. Poisson's ratios were determined by sonic measurements on pastes made from cement A cured 1 week. They ranged from 0.27 for a specimen of nominal water-cement ratio 0.25 to a value of 0.31 for a specimen of nominal water-cement ratio 0.7. Adams and Williamson [28] have concluded that Poisson's ratio for plutonic rocks is approximately 0.27. These rocks are silicates and have essentially the same compressibility as hydrated portland cement. In table 15 elastic constants are

TABLE 15. Elastic constants for the hydrated cements, estimated from compressibility measurements, assuming Poisson's ratio = 0.27

	1 to 5,000 atm	5,000 to 10,000 atm
Young's modulus.....	4.5×10^5 atm 6.6×10^6 lb/in. ² 4.6×10^5 kg/cm ²	6.3×10^5 atm 9.3×10^6 lb/in. ² 6.5×10^5 kg/cm ²
Modulus of shear.....	1.8×10^5 atm 2.6×10^6 lb/in. ² 1.9×10^5 kg/cm ²	2.5×10^5 atm 3.7×10^6 lb/in. ² 2.6×10^5 kg/cm ²
Compressibility.....	3.1×10^{-6} atm ⁻¹ 2.1×10^{-7} in. ² /lb 3.0×10^{-6} cm ² /kg	2.2×10^{-6} atm ⁻¹ 1.5×10^{-7} in. ² /lb 2.1×10^{-6} cm ² /kg

given for dried cement pastes. The values for Young's modulus and shear modulus have been computed from the average value of compressibility, assuming a Poisson's ratio of 0.27. It may be noted that these elastic constants of cement are nearly the same order of magnitude as corresponding constants of the more compressible rocks, many of which are used as aggregates in concrete [5, 28].

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