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THE DIMENSIONAL INSTABILITY OF HEATED PORTLAND CEMENT CONCRETE

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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The Ohio State University
1970

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"Heat Resistant Concrete for Prestressed-Concrete-Pressure-Vessel

"The Effects of Moisture Content on the Structural Properties of
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"The Effects of Exposure to Elevated Temperatures on the Time-Dependent
Strains in Concrete." Proceedings of the First International
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NOMENCLATURE

\( V_{hc} \), Hydrated cement in cement paste, volume percent
\( V_{uc} \), Unhydrated cement in cement paste, volume percent
\( V_{pt} \), Total porosity in cement paste, volume percent
\( V_{pc} \), Capillary porosity in cement paste, volume percent
\( V_{pg} \), Gel porosity in cement paste, volume percent
\( P_{t} \), Total porosity of cement paste, cc
\( P_{c} \), Capillary porosity of cement paste, cc
\( V \), Bulk volume of cement paste, cc
\( d_{p} \), Bulk density of saturated cement paste, gms/cc
\( w_{e} \), Evaporable water content of cement paste, gms
\( w_{c} \), Capillary water content of cement paste, gms
\( w_{g} \), Gel water content of cement paste, gms
\( w_{n} \), Non-evaporable water content of cement paste, gms
\( w_{t} \), Total water content of cement paste, gms
\( \Delta w_{t} \), Weight loss (water) of cement pastes due to heating, gms
\( m \), Weight of saturated cement paste, mortar, or concrete specimen, gms
\( c \), Weight of cement in a specimen of cement paste, mortar, or concrete, gms
\( \phi \), Specific surface area of cement paste as measured by nitrogen gas adsorption, \( \text{m}^2/\text{gm} \)
\( L_{o} \), Initial length of cement paste, mortar, or concrete specimen in saturated state, prior to study, cm
\( L \), Length of cement paste, mortar, or concrete specimen at any time during the period of study, cm
NOMENCLATURE (CONTINUED)

$\Delta L$, Change in length of cement paste, mortar, or concrete specimen at any time during the period of study, $(L_0 - L)$, cm

$\epsilon_{wn}$, Linear contraction accompanying the loss of non-evaporable water from heated cement paste, percent of original length

$\epsilon_{we}$, Linear contraction accompanying the loss of evaporable water from heated cement paste, percent of original length

$\alpha$, Coefficient of linear thermal expansion of cement paste or concrete, percent per °F

$\left[ \frac{\Delta L}{L_0} \right]^*$, Measured linear deformation of heated paste or mortar specimen at point where all evaporable water is removed, percent of original specimen length

$\epsilon_{wn}^*$, Total linear contractive deformation accompanying the loss of non-evaporable water from heated cement paste or mortar, percent of original length

$\epsilon_{tot}$, Permanent linear contraction at room temperature of pastes or mortars exposed to 500 °F for 48 hours, percent of original length

Blaine Fineness, An index of the mean particle size of cement powder as determined in ASTM C204-55, cm$^2$/gm

$\mu$ in, $1 \times 10^{-6}$ inches (microinch)

x
INTRODUCTION

Portland cement concrete is without doubt the most widely used construction material in the world today. The intensive use of concrete in structures and pavements has, over the years, provided the stimulus for the generation of a wealth of information concerning the engineering properties of this material under normal use conditions. Until recently there has been relatively little interest in the effects of heat exposure on the engineering properties of concrete. Prior to 1956, the main stimulus for studies on the effects of heat exposure on concrete came from the need to generate an understanding of the fire resistance of concrete. Fires in structures produce an environment of high heat flux for relatively short times on massive, well matured, unsealed concrete members. Investigations into the fire resistance of concrete usually have been designed to recreate these environmental parameters in the laboratory.

The use of concrete in nuclear reactors, particularly as the primary containment vessel in prestressed-concrete-pressure-vessel-reactors (PCPVR), has focused attention on the lack of information on the effects of sustained, relatively low temperatures on the engineering properties of concrete. It is common practice to provide costly insulation and cooling systems in a PCPV to hold the maximum temperature below about 170 F. This arbitrary temperature limitation
is based on available data which predicts strength losses with increasing temperatures in concrete. Although progress has been made in the use of portland cement concrete in PCPV reactors, the full versatility and economy of this material has not been realized. Engineering data are needed for concrete subjected to the unique environment of the PCPVR to define the maximum operating temperature for conventional concrete and to direct the formulation of improved concretes capable of fail-safe operation at higher temperatures. It is of particular interest to learn the effects of sustained, moderately intense heat exposure on the strength and dimensional stability of portland cement concrete.

From July, 1967, through January, 1969, the author was involved in a study of the effects of heat exposure on portland cement concrete as related to its use in a PCPVR. The results of this study, which have been published, provided strong evidence that the most important single event influencing the dimensional instability of heated portland cement concrete was the loss of water, both evaporable and chemically combined, from the cement paste phase. It was felt that a study of the factors controlling the dimensional instability of heated cement paste represented the most logical next step in the attempt to elucidate the effects of heat exposure on the dimensional instability of portland cement concrete.

The present investigation was undertaken with the following broad aims in view:

1. To study the nature of the inelastic deformation behavior of heated cement paste to examine under closely
controlled conditions the behavior of that portion of concrete believed to affect primary control over its dimensional instability.

2. To develop a better understanding of the mechanisms involved in the dimensional instability in concrete.

3. To define the role of temperature regarding the dimensional instability of portland cement concrete.

4. To define the influence of the aggregate phase regarding the dimensional instability of heated portland cement concrete.
I. TECHNICAL DISCUSSION

Characterization of Concrete

Typical concrete mixes contain 60 to 75 volume percent aggregate, 7 to 15 volume percent cement, 14 to 21 volume percent water, and 0.5 to 8 percent of entrained air. Concrete becomes rigid by reaction of the cement with water to form a highly cementitious binder. The cement reaction products are comprised of about 50 weight percent of calcium silicate hydrate (referred to as tobermorite gel) and 25 weight percent calcium hydroxide, with the remainder being calcium aluminoferrite hydrate, tetracalcium aluminate hydrate, and calcium monosulfoaluminate. The cement reaction products are collectively referred to as cement gel. Cement gel plus the entrained air and porosity in concrete is referred to as cement paste.

In a monumental study published in 1946-1947, Powers and Brownyard provided a comprehensive and detailed picture of the structure of hardened cement paste. The pore system in hardened cement paste is unique—in fact, two distinct pore systems have been identified, viz., capillary pores and gel pores. Capillary pores are voids that were originally water-filled spaces in the initial mixture of cement and water. The size of these voids in hardened paste has been

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*The term cement refers to portland cement.
determined to be about 100 to 2000 Å. The amount of capillary porosity in a paste is controlled by the water/cement ratio. At any given curing age, a paste with a higher initial water/cement ratio will have a greater capillary porosity than one with a lower starting water/cement ratio. Gel pores are voids inherent in the cement gel, i.e., spaces between individual gel particles in the coherent gel structure. Gel pores are one or two orders of magnitude smaller than capillary pores (20 to 40 Å). The lowest possible amount of gel porosity is about 26 volume percent in an air-free, fully matured paste. This sets a minimum porosity value on cement pastes prepared by conventional means. A simplified model of the structure of cement paste is shown in Figure 1.

The water in cement paste exerts a tremendous influence on the properties of the paste. This water is of two types, viz., evaporable and nonevaporable. Evaporable water is arbitrarily defined as water having a vapor pressure greater than 0.5μ and nonevaporable water is defined as water having a vapor pressure less than 0.5μ. The nonevaporable water is equated to the chemically combined water of the solid hydrate phases and Ca(OH)_2. In terms of the gel structure the evaporable water is water contained in the gel and capillary pores of the paste and is identified as gel water and capillary water, respectively.

The cohesiveness of cement paste (its ability to function as a cementitious binder) is directly related to the extensive surface area of the cement gel (300 m²/gm. in fully hydrated pastes). The
Figure 1. Simplified model of the structure of hardened cement paste. Gel particles are represented as needles or plates; C designates capillary cavities. Ca(OH)$_2$ crystals, unhydrated cement, and minor hydrates are not represented.
nature of the bonding between colloidal gel crystallites may be either physical or chemical.\textsuperscript{9,10} The strength of hardened cement paste varies in direct proportion to a factor designated as the "gel-space" ratio.\textsuperscript{11} This ratio is the volume percent of gel occurring in a unit volume of paste—the remaining volume being taken up by porosity. This empirical relationship is shown in Figure 2.

The Dimensional Instability of Concrete
Under Normal Ambient Conditions

Concrete exhibits considerable dimensional instability in normal service environments due to the effects of creep (inelastic volume changes associated with the presence of external stress), shrinkage and swelling (volume changes associated with changes in the amount of water in the cement paste), and thermal expansion. All of these factors produce deformation in the concrete in response to parameters of the service environment, e.g. stress, relative humidity and normal changes in ambient temperature.

It has been demonstrated\textsuperscript{12} that creep and shrinkage are intimately related phenomena. This fact is rendered quite evident when viewed in terms of their similar behavior and response to changes in external parameters, e.g.,

1. Both shrinkage and creep in concrete have been shown to be primarily controlled by the hardened cement paste phase.

2. Both shrinkage and creep when operative for the first time produce deformations that are partly recoverable and partly irrecoverable.
Figure 2. Relationship between compressive strength and gel-space ratio for cement-sand mortars.
3. The evaporable water phase in hardened cement paste has been shown to play a dominant role in both shrinkage and creep.

Typical shrinkage behavior exhibited by cement paste during the loss of evaporable water is depicted in Figure 3. The discreet steps in the shrinkage-weight loss curve are attributed to the removal of four types of evaporable water from the pastes. The water coming off initially from the saturated paste is present in the macropores of the paste (air voids, and perhaps large capillary pores) and its removal does not produce significant shrinkage inasmuch as it is present in the paste as unadsorbed bulk water. Water coming off when the relative humidity is decreased from 0.90 to 0.35 is believed to be that held by capillary condensation in the paste. Its removal produces a large shrinkage due to capillary tension stress which serves to draw together solid gel surfaces in mutual contact with a given volume of water. The water lost as the relative humidity is decreased from 0.35 to 0.20 accompanies the destruction of concave menisci and causes little shrinkage. The last remnants of water to be removed as the relative humidity is decreased below 0.2 is intercrystalline and intracrystalline adsorbed water and hydrate water. Its removal is accompanied by a large shrinkage as solid gel surfaces previously separated by water meet and coalescence and, in addition, collapse of the microcrystals of gel due to loss of interlayer water is effected. Recoverable or reversible shrinkage is that portion of the total shrinkage that is recovered when the paste is resaturated with water. About 20 percent of the original shrinkage deformation is irrecoverable.
Figure 3. Relationship between weight loss and shrinkage of hardened cement paste.
The effect of the presence of an external compressive stress during the drying of concrete is to increase the rate and magnitude of the contractive deformation. It is common practice* to define creep as the average total strain (per psi) at any time in a loaded specimen minus the average drying shrinkage strain (per psi) in an "identical" specimen that is not loaded. For applied stress levels up to about 40 percent of ultimate compressive strength, the creep at any given time and the magnitude of irrecoverable creep is roughly in linear proportion to the stress.** Excellent discussions concerning the mechanisms of drying shrinkage** and creep** in concrete have been published.

Most materials exhibit an increase in absolute volume when their average temperature is increased. If the material does not undergo any irreversible chemical or physical change, it will contract to its original geometry when the original temperature is re-established. Concrete and hardened cement paste heated in the normal ambient temperature range (0 to 100 F) are no exception. When measuring the thermal expansion of concrete, it is necessary to seal the specimen to prevent the loss of moisture that would normally occur on heating and to insure that the physical and chemical makeup of the concrete remains unchanged for the duration of the test. As with other concrete property responses, the thermal expansion behavior of concrete at normal ambient temperatures reflects the behavior of the hardened

*ASTM C512-66T Tentative Method of Test for Creep on Concrete in Compression.
cement paste phase. The linear coefficient of thermal expansion of hardened cement paste has been shown to depend on the amount of evaporable water in the paste at the time of testing \(^{18-20}\). Minimum expansion values (6 to 7 \(\mu\) in. per in. per °F) are exhibited by saturated pastes and by relatively dry pastes. Pastes containing water between these extremes exhibit high thermal expansion (9 to 11 \(\mu\) in. per in. per °F). Concrete exhibits similar thermal expansion behavior although the difference between the maximum values and the minimum values is not as pronounced as with the pastes inasmuch as the presence of aggregate restrains the movement of the paste. Dimensional changes exhibited by unsealed concrete or cement paste when subjected to temperatures considerably above normal ambient are more complex than the simple thermal expansion just discussed and will be considered subsequently.

**The Effects of Heat Exposure on Concrete**

**Chemistry**

Differential thermal and thermal-gravimetric investigations \(^{21-23}\) of portland cement hydration provide a convenient illustration of the reactions that can be expected to occur in fully hydrated cement paste heated in air at atmospheric pressure. Drawing on these published data, a representative DTA of hardened portland cement paste is shown in Figure 4. A broad endotherm is observed beginning at less than 212 F, reaching a maximum at slightly above 212 F, and continuing up to 842 F. The initial portion of the
endotherm is due to the removal of free (evaporable) water from the cement paste. Dehydration and dehydroxylation of the various hydrated cement phases as well as continued loss of evaporable water account for the endotherm from 212 to 842 °F. The approximate peak temperature of the various phases contributing to this endotherm are shown in Figure 4. Tobermorite gel and hydrated calcium sulfoaluminate are the first solid phases affected. The pronounced endotherm between 932 and 1112 °F is due to the decomposition of Ca(OH)₂. An endotherm sometimes observed at around 1472 °F is due to the decomposition of CaCO₃ which may be present as a result of carbonation of Ca(OH)₂ by atmospheric CO₂.

The order in which the various types of evaporable water are removed by heating is expected to be similar to that effected by a reduction in relative humidity at normal temperatures. The removal of chemically combined water from cement paste is an irreversible process and may not be completed until temperatures in excess of 1000 °F have been reached.²⁴

Most of the natural aggregates used in structural grade concrete are stable up to 500 °F and possibly well beyond this temperature, i.e., they exhibit no chemical or phase transformations that could cause disruptive volume changes or strength losses. Although reactions between the cement and aggregate phases in unsealed concrete heated to temperatures as high as 500 °F cannot be ruled out completely, it is likely that, because of the combined effects of the relatively large size of the aggregate particles, the absence of free moisture above 250 °F, the relatively low temperature levels, and the inherent chemical
stability of the aggregate at these temperatures, the potential for such reactions is not great.

**Engineering Properties of Concrete**

Data compiled by a number of investigators on the compressive and flexural strength of cement, mortar, and concrete as influenced by exposure to temperatures up to 1000 F are shown graphically in Figures 5 and 6, respectively. The envelope surrounds the extremes of reported measurements, while the average of the data is shown as a dashed line. All values for heated specimens were calculated as a percentage of the as-cured strength to establish a common reference for the various studies. Included in the Figures are a number of test variables that are placed on the graphs so as to indicate their relative influence on the test results.

Under some testing conditions where the free water was not contained, the compressive strength of concrete heated as high as 600 F was actually enhanced relative to the as-cured unheated value. Alternatively, specimens whose free moisture was contained during heating exhibited significant losses in compressive strength at relatively low temperatures. Concrete heated above about 600 F invariably suffered a deterioration in compressive strength. Almost without exception, the flexural strength of concrete is adversely affected by exposure to temperatures much above normal ambient. The rate of flexural strength deterioration is apparently highest at temperatures above about 400 F.

It has been adequately demonstrated that exposure to elevated temperatures causes a reduction in the elastic modulus of
Figure 5. Extremes of the influence of heat exposure on the compressive strength of concrete.
Figure 6. Extremes of the influence of heat exposure on the flexural strength of concrete.\textsuperscript{25-31}
concrete. Data from these studies are plotted in Figure 7 as the extremes and average measured values relative to unheated control specimens. At temperatures up to about 600 F the elastic modulus appears to be the structural property of concrete most sensitive in terms of loss of initial value to the effects of heat exposure.

It may be expected that the exposure of concrete to elevated temperatures will accelerate the rate of shrinkage inasmuch as the rate of evaporable water loss will be accelerated. However, consideration must also be given to the fact that while the heated concrete is undergoing shrinkage, it is simultaneously expanding due to thermal expansion. At temperatures much above 212 F, nonevaporable water will be lost from the cement paste. Very few experimental data are available which show how this latter event affects the dimensional stability of concrete; although Powers\(^5\) predicted that the loss of nonevaporable water would produce a shrinkage in cement paste.

Unstressed concrete on first heating from a saturated state exhibits an expansion\(^{35,36}\); although if the temperature level is not too high and the heat is sustained, the concrete may eventually exhibit a shrinkage.\(^{37}\) Most concretes heated below about 400 F exhibit a permanent shrinkage on cooling to room temperature while exposure to temperatures much above 400 F produces a permanent expansion. However, concrete prepared with low density aggregate (expanded slag or vermiculite) exhibits a permanent shrinkage after all heat exposures. The expansion exhibited by concrete during first heating appears to be in proportion to the coefficient of thermal expansion of the aggregate.
Modulus of Elasticity, Percent of as-cured, unheated reference value

Temperature of Heat Exposure, F

Figure 7. Extremes of the influence of heat exposure on the modulus of elasticity of concrete.
as shown in Table 1.

The deformation behavior of hardened cement pastes on initial exposure to elevated temperatures has been studied relatively little. Very interesting thermal dilation data have been reported for Type III portland cement paste and concrete. Hardened paste heated for the first time exhibited an initial expansion on heating to 400-500 °F, then a subsequent contraction on further heating to 1500 °F. The deformation at a given temperature as well as the magnitude of the permanent contraction on cooling was influenced by the heating rate as shown in Figure 8. The lower heating rate produced a lesser permanent contraction than the higher. The initial thermal deformation curve of a vermiculite concrete containing Type III portland cement is shown in Figure 9 which shows data for concretes having different cement contents. The dimensional change of the concretes at almost all temperatures and the permanent dimensional change on cooling was a contraction. The shrinkage at any given temperature was greater for the concrete containing the highest proportion of cement. The fact that the magnitude of thermal deformation and permanent dimensional change of the paste is sensitive to the heating rate rules out the possibility that the thermal expansion of concrete can be viewed simply as an additive effect of the expansion of the aggregate and shrinkage of the paste.

The effect of external stress on the deformation (creep) of heated concrete has been studied. There is general agreement that the amount and rate of creep deformation in concrete is increased
<table>
<thead>
<tr>
<th>Rock Group</th>
<th>Typical Silica Content Percent, By Weight</th>
<th>Thermal Expansion Coefficient of Aggregate Microstrain/°F</th>
<th>Maximum Variation</th>
<th>Mean</th>
<th>No. of Rock Specimens Tested</th>
<th>Thermal Coefficient of Expansion of Concrete, Microstrain/°F</th>
<th>Minimum Recorded</th>
<th>Maximum Recorded</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chert</td>
<td>94</td>
<td>4.1 7.2</td>
<td>3.1</td>
<td>6.7</td>
<td>50</td>
<td>6.3 6.8</td>
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<tr>
<td>Quartzite</td>
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<td>3.4</td>
<td>5.7</td>
<td>28</td>
<td>6.5 8.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quartz</td>
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<td>...</td>
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<td>Sandstone</td>
<td>84</td>
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<td>5.2</td>
<td>43</td>
<td>5.1 7.4</td>
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<td></td>
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<td>Marble</td>
<td>Negligible</td>
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<td>10.1</td>
<td>0.7</td>
<td>35</td>
<td>2.3 4.1</td>
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<tr>
<td>Siliceous</td>
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<td></td>
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<td>Limestone</td>
<td>45</td>
<td>2.0 5.4</td>
<td>3.5</td>
<td>4.6</td>
<td>6</td>
<td>4.5 6.1</td>
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<td></td>
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<tr>
<td>Granite</td>
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<td>5.6</td>
<td>3.8</td>
<td>79</td>
<td>4.5 5.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolerite</td>
<td>50</td>
<td>2.5 4.7</td>
<td>2.2</td>
<td>3.8</td>
<td>4</td>
<td>...</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basalt</td>
<td>51</td>
<td>2.2 5.4</td>
<td>3.2</td>
<td>3.6</td>
<td>18</td>
<td>4.4 5.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limestone</td>
<td>Negligible</td>
<td>-1.0 6.5</td>
<td>7.5</td>
<td>3.0</td>
<td>125</td>
<td>2.4 5.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gravel</td>
<td>5-95</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 8. Effect of heating rate on the initial thermal expansion of Type III portland cement paste.
Figure 9. Initial thermal expansion of vermiculite concretes containing Type III portland cement.
monotonically with increased temperature. Limited experimental data and the wide range of test procedures used make it difficult to draw other than general conclusions regarding the nature of the phenomenon. Measurements of creep in unsealed, heated concrete are complicated by the fact that moisture is being lost continually during the test. This means that drying shrinkage is contributing a component of the total deformation; hence it must be isolated and measured if the creep component is to be identified. In addition, if deformation is measured during the rise in temperature to the desired level, thermal expansion strain must be considered. The creep of dry concrete at room temperature reportedly is nil. 44,49

The results 1,3 of studies by the author of time-dependent deformation in stressed and unstressed concrete heated to temperatures up to 500 F are presented in Figures 10 through 12. The data are presented as cumulative linear deformation (calculated as percent of the original specimen length) versus test duration in days. The complete history of any specimen can be determined by references to the appropriate legends for the Figures.

The overall heating and loading histories of the two concretes studied were different. However, for the portions of the study when loading and heating histories were identical, the gravel and limestone concrete responded about the same to the imposed test conditions. Unstressed concrete heated for the first time to 250 or 500 F exhibited an initial and continuing expansion. Concrete stressed (40 percent of ultimate compressive strength) before heating was begun
Figure 10. Deformation of stressed and unstressed limestone concrete heated to 250 F.
Figure 11. Deformation of stressed and unstressed gravel concrete heated to 250 and 500°F.
Figure 12. Deformation of limestone concrete heated to 500 F.\textsuperscript{1,3}
exhibited a contraction on subsequent heating. The sign (contraction or expansion) and magnitude of the measured specimen deformation at any given time were dependent on the temperature of the specimen, on whether or not the specimen was loaded; and on the time in the specimen's heating history when the load was applied.

The fact that the time-dependent deformation exhibited by heated concrete is influenced by the time in the concrete's heating history in which the load is applied suggests that the various deformation mechanisms operative in heated, stressed concrete do not operate independently: they are interdependent variables. Thus, superposition of the effects of the deformation mechanisms in heated, stressed concrete is not possible. It was concluded that the loss of water, both evaporable and nonevaporable (chemically combined), from the cement paste phase is probably the most important single event influencing the inelastic deformations of heated concrete. The role assumed by stress in modifying the deformational behavior of heated concrete appeared to be closely linked to the loss of water from the concrete.
II. LABORATORY INVESTIGATION OF THE EFFECTS
OF HEAT EXPOSURE ON THE DIMENSIONAL
STABILITY OF HARDENED CEMENT PASTE

This study was undertaken to investigate in greater detail the role played by the cement paste phase relative to the dimensional instability exhibited by portland cement concrete on exposure to temperatures up to 500 F. An experimental program was planned in which simultaneous measurements were made of dimensional change and weight loss in cement pastes during heating. Corollary analyses permitted the weight loss data to be interpreted in terms of the removal of evaporable and nonevaporable water from the pastes. The effect of paste porosity on the dimensional stability was examined using pastes prepared with different water/cement ratios. Changes in the paste microstructure as influenced by heat exposure were also studied. The effect of aggregate on the behavior of heated concrete was studied in greater detail using a specially formulated mortar composed of 50 v/o cement paste and 50 v/o of monosized quartz grain.

Materials and Compositions

A Type I portland cement* was selected for the study. The cement was of commercial origin and had a Blaine fineness of *Columbia portland cement, Type I.
3540 cm$^2$/gm. One 94 pound bag of the cement furnished more than enough material for preparation of all of the specimens used in the study. A Type I cement was chosen in view of the predominant use of this cement by the industry with a resultant abundance of available property data. It was not expected that any major difficulties would be experienced in attempting to extrapolate the results of the present study to include other sources of Type I cement or other types (II, III, IV, V) of portland cement. The aggregate used in the preparation of some of the specimens was a carefully sized (20 to 30 mesh) rounded quartz grain from Ottawa, Illinois.

Four basic mixes were prepared for study:

1. Cement paste (water plus cement) with a water to cement weight ratio (w/c) of 0.33.
2. Cement paste with a w/c ratio of 0.45.
3. Cement paste with a w/c ratio of 0.60.
4. Mortar composed of 50 volume percent quartz grain and 50 volume percent cement paste. The cement paste phase in the mortar had a w/c ratio of 0.45.

Specimens in the shape of right circular cylinders (5/8 inch diameter by 4-7/8 inch long) were prepared of all the mixes by casting into glass test tubes. A description of the specimen preparation technique is given in Appendix A.

**Equipment and Technique**

Simultaneous measurements of dimensional change and weight loss were obtained on cement paste and mortar specimens during dynamic and static heating conditions at temperatures up to 500 F. The apparatus
used to obtain these measurements is shown schematically in Figure 13. Cylindrical specimens were suspended from a bottom-loading Mettler balance (Model P1200 which had a readability of 0.01 gram) using a small brass chain of about 18 inches in length. The chain was attached to the specimen by means of a steel eyelet which was cemented in the top of the specimen. The specimen thus suspended was positioned in the center of a triangular-shaped furnace that was fabricated using three large rectangular (12 inches by 6 inches) Nichrome spring heating elements. In addition to the large side elements the furnace also had cartridge type heaters in the top and bottom insulation. This heating arrangement afforded a large constant temperature zone in the furnace. Specimen temperature was monitored by three Chromel-Alumel thermocouples placed at the top, center, and bottom of the specimen which were wired in parallel so that an average temperature could be recorded with one potentiometer reading. The temperature gradient along the specimen did not exceed 5 F once the specimen was at temperature and was usually less than 2 F. During heating or cooling periods the gradient along the length of the specimen did not exceed 10 F. The heating schedules used in the study were achieved through predetermined manual increases in a variable output stepdown transformer. Isothermal conditions were achieved using a Foxboro potentiometer controller.

Specimen deformation was measured remotely using a Gaertner double telescope optical extensometer. The telescopes, with a focal length of about 12 inches, were mounted so that the fixed cross hairs were 10 cm. apart. The movement of reference marks on the specimen was
Figure 13. Schematic drawing of the apparatus used to perform simultaneous measurements of weight loss and deformation in unstressed cement paste and mortar specimens during heating to 500 F.
then measured relative to the fixed cross hairs using a vernier micro-
meter linked mechanically to movable cross hairs in each telescope.
The verniers could be read to the nearest $10^{-5}$ cm. The precision of
the method in terms of the operator's ability to superimpose the
movable cross hairs on the specimen reference marks was determined to
be $\pm 3 \times 10^{-4}$ cm. The 95 percent confidence interval* on the deformation
values, which are presented in terms of percent of original specimen
length, is $\pm 0.006$ percent. The "+"-shaped reference marks were in-
scribed on the specimen 10 cm. apart using a razor blade knife. A
0.7 mil wire was cemented into the horizontal reference mark (using
sodium silicate solution) to provide for more accurate sighting on the
specimen. A photograph of a cylindrical paste specimen as used in this
study is shown in Figure 14.

A double check on the weight loss and strain data was obtained
by independent "before and after" measurements of specimen weight on an
analytical balance (digital readout to 0.0001 gram) and measurements of
specimen deformation using a 4 to 5 inch vernier micrometer (readout to
0.0001 inch) in conjunction with a jig for positioning the specimen.

* Ninety-five percent C.I. using twenty data points.
Figure 14. Photograph of cement paste specimen used in the study (1.7X)
Experimental Procedure

Measurements of Weight
Loss and Dimensional
Change in Heated Specimens

Cement paste and mortar specimens were heated to 500 F under atmospheric pressure using four different heating schedules which are described below.

Schedule A

This heating schedule was intended to provide for a slow removal of evaporable water at low temperatures (<250 F). Saturated specimens were heated from room temperature to 180 F in 12 hours (~9 F per hour), held at 180 F for 12 hours, heated from 180 F to 250 F in 8 hours (~9 F per hour), held at 250 F for 18 hours, heated from 250 F to 500 F in 3 hours (~83 F per hour); then held at 500 F for 19 hours before cooling. Total heating time was 72 hours.

Schedule B

This heating schedule provided a rapid increase in specimen temperature to 250 F with a hold at 250 F to effect a removal of evaporable water before subjecting the specimen to further increases in temperature. Saturated specimens were heated rapidly to 250 F from room temperature in about 2 hours (~90 F per hour), held at 250 F for 22 hours, heated from 250 F to 500 F in 2-3/4 hours (~90 F per hour); then held at 500 F for 22 hours before cooling to room temperature. Total heating time was 48 hours.

Schedule C

This heating schedule provided a rapid and direct heat-up to 500 F from room temperature so as to cause a significant increase in the temperature of the specimen while it still contained large quantities of evaporable water. Saturated specimens were heated from room temperature to 500 F in 4-3/4 hours (~90 F per hour),
then held at 500 F for 44* hours before cooling to room temperature. Total time of heating was 48-3/4 hours.

Schedule C

This heating schedule was intended to show the effect of prior removal of the evaporable water from the pastes on their deformational behavior during subsequent heating. Specimens processed under this schedule were first subjected to a five day vacuum drying period which removed most of the evaporable water. Specimens thus treated were heated directly to 500 F from room temperature in 4-3/4 hours (~90 F, same as Schedule C) and held at 500 F for 44* hours before cooling to room temperature. Total heating time was 48-3/4 hours.

Measurements of specimen temperature, length change and weight change were made continuously during the testing of the specimen. During periods of temperature increase or periods of rapid change in specimen weight and/or length, measurements were made every ten minutes. Forty to seventy separate measurements were recorded during any given test. At the conclusion of the 500 F soak time the specimens heated according to all four schedules were cooled to room temperature in increments of 100 F.

Paste Characterization Studies

The cement pastes used in the study were examined prior to and following their exposure to temperatures up to 500 F to determine the effect of heat exposure on:

1. The evaporable water content.
2. The nonevaporable water content.
3. The specific surface area.

*The 0.33 paste was held at 500 F for 24 hours instead of 44.
In addition, the pastes were characterized prior to heating to determine:

4. The volume percent of each phase, including porosity making up the paste.

5. Paste density.

The analytical work was carried out on cylindrical specimens that had been cured for the approximate same period of time as were the specimens used in the deformation studies, i.e., 60-80 days. The procedures used in this work are discussed in detail in Appendix B.

Experimental Results

Characterization of As-Cured Pastes

Data regarding the composition and properties of the as-cured cement pastes used in the study at the time of testing (before any heat exposure) are presented in Table 2 and shown graphically in Figures 15 and 16.

Results obtained in the density measurements indicate that the cylindrical specimens were quite homogeneous throughout their length. The increase in paste maturity factor with increased w/c ratio indicates that more of the cement was hydrated in the specimens containing higher starting water contents. For the curing conditions used in this study this result is to be expected.
<table>
<thead>
<tr>
<th>Paste Identification</th>
<th>Paste Composition, Volume Percent</th>
<th>Paste Porosity Volume Percent</th>
<th>Water Content</th>
<th>Paste Density, gms/cc. Section (Cylinder)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydrated Cement ( V_{hc} )</td>
<td>Unhydrated Cement ( V_{uc} )</td>
<td>Capillary Porosity ( V_{pc} )</td>
<td>Gel Porosity ( V_{pg} )</td>
</tr>
<tr>
<td>0.33</td>
<td>.498</td>
<td>.212</td>
<td>.290</td>
<td>.107</td>
</tr>
<tr>
<td>0.45</td>
<td>.517</td>
<td>.126</td>
<td>.357</td>
<td>.168</td>
</tr>
<tr>
<td>0.60</td>
<td>.481</td>
<td>.071</td>
<td>.448</td>
<td>.261</td>
</tr>
</tbody>
</table>

(a) Average of measurements on 4 different specimens.
(b) Average of measurements on 10 different specimens.
Figure 15. Porosity of hardened cement pastes at time of testing.
Figure 16. Water content of hardened cement pastes at time of testing.
The total porosity varied from 29 percent by volume in the 0.33 pastes to about 45 percent by volume in the 0.60 pastes. The capillary porosity represented 37 percent of the total porosity in the 0.33 pastes, 47 percent in the 0.45 pastes; and 58 percent in the 0.60 pastes. The calculations indicate that the volume percent of hydrated cement phase (gel) was nominally the same in all the paste specimens (48-50 volume percent) regardless of the initial water/cement ratio. The volume percent of anhydrous (unreacted) cement, however, increased from about 7 percent in the 0.60 pastes; to 13 percent in the 0.45 paste; to 21 percent in the 0.33 paste. If it is assumed that all the gel pores are completely water filled and that the remainder of the evaporable water is present in the capillary pores, and if it is further assumed that the specific volume of the evaporable water is 0.9950, then it can be shown that the distribution of the evaporable water in the as-cured pastes was as shown in Table 3.

*In subsequent text the cement paste specimens used in this study will be designated by reference to their initial water/cement ratio, i.e., the 0.33 paste was prepared using a water/cement ratio of 0.33; the 0.45 paste was prepared using a water/cement ratio of 0.45; and the 0.60 paste was prepared using a water/cement ratio of 0.60.
TABLE 3

DISTRIBUTION OF EVAPORABLE WATER IN AS-CURED CEMENT PASTES

<table>
<thead>
<tr>
<th>Cement Paste</th>
<th>Volume Percent of Evaporable Water ($w_e$) in the Gel Pores</th>
<th>Volume Percent of Evaporable Water ($w_e$) in the Capillary Pores</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>65.6</td>
<td>34.4</td>
</tr>
<tr>
<td>0.45</td>
<td>55.7</td>
<td>44.3</td>
</tr>
<tr>
<td>0.60</td>
<td>46.6</td>
<td>53.4</td>
</tr>
</tbody>
</table>

Effect of Heat Exposure on Specific Surface Area of Hardened Cement Pastes

Measurements of the specific surface area of the cement pastes before and after a 48 hour exposure to temperatures of 175, 250, 375, and 500 F are shown in Table 4 and presented graphically in Figure 17. A significant reduction in surface area was caused by heating the pastes to 175 F; although exposure of the pastes to higher temperatures (250, 375 and 500 F) did not result in any further reduction. The decrease in surface area caused by heating (relative to the original surface area) varied for the pastes as is seen in Table 5. Only 35 percent of the surface area of the dense, low porosity 0.33 paste remained accessible to nitrogen molecules following the heat exposure. Over half of the surface area of the low density, more porous 0.60 paste remained accessible to nitrogen molecule adsorption after heat exposure. In fact, a linear relationship exists between capillary porosity of the paste and the reduction in surface area of...
# Table 4

**Surface Area Measurements of As-Cured and Heated Cement Pastes**

<table>
<thead>
<tr>
<th>Paste Specimen Identification</th>
<th>Water/Cement Ratio</th>
<th>As-Cured Surface Area m²/gm.</th>
<th>Surface Area After 48 Hours at Indicated Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>175 F H.T.</td>
</tr>
<tr>
<td>H-17</td>
<td>0.33</td>
<td>21.3</td>
<td>6.6</td>
</tr>
<tr>
<td>J7</td>
<td>0.45</td>
<td>23.0</td>
<td>7.5</td>
</tr>
<tr>
<td>H-5</td>
<td>0.45</td>
<td>24.2</td>
<td>8.6</td>
</tr>
<tr>
<td>J-5</td>
<td>0.45</td>
<td>25.2</td>
<td>9.8</td>
</tr>
<tr>
<td>4-1-17</td>
<td>0.45</td>
<td>Avg. 23.1</td>
<td></td>
</tr>
<tr>
<td>4-27</td>
<td>0.45</td>
<td>52.7</td>
<td>16.3</td>
</tr>
<tr>
<td>4-17</td>
<td>0.45</td>
<td>43.1</td>
<td>23.2</td>
</tr>
<tr>
<td>4-15</td>
<td>0.45</td>
<td>41.4</td>
<td>17.3</td>
</tr>
<tr>
<td>4-25</td>
<td>0.45</td>
<td>54.4</td>
<td>21.8</td>
</tr>
<tr>
<td>4-45</td>
<td>0.45</td>
<td>Avg. 48.4</td>
<td>24.5</td>
</tr>
<tr>
<td>6-2</td>
<td>0.60</td>
<td>51.1</td>
<td>24.8</td>
</tr>
<tr>
<td>6-3</td>
<td>0.60</td>
<td>Avg. 49.8</td>
<td>24.8</td>
</tr>
<tr>
<td>6-2X</td>
<td>0.60</td>
<td>50.3</td>
<td>24.8</td>
</tr>
<tr>
<td>6-3X</td>
<td>0.60</td>
<td>46.6</td>
<td>24.8</td>
</tr>
</tbody>
</table>

*Note: Surface Area values are in m²/gm.*
Figure 17. Effect of 48 hour heat exposure on specific surface area of hardened cement pastes.
the paste on heating.

**TABLE 5**

<table>
<thead>
<tr>
<th>Cement Paste</th>
<th>Specific Surface Area of Pastes After 48 Hour Exposure at 175, 250, 375, or 500 F, Percent of Original Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>35.0</td>
</tr>
<tr>
<td>0.45</td>
<td>43.8</td>
</tr>
<tr>
<td>0.60</td>
<td>55.4</td>
</tr>
</tbody>
</table>

**Effect of Heat Exposure on Evaporable and Nonevaporable Water Content of Hardened Cement Paste**

The changes in the water content of the cement pastes on heating for 48 hours at 250 and 500 F are given in Table 6 and are shown graphically in Figure 18. After heating for 48 hours at 250 F the evaporable water \( w_e \) was completely removed from all the pastes studied. A relatively small amount of the chemically combined water \( w_n \) was removed from the pastes at this temperature. Significant quantities of chemically combined water \( w_n \) were lost from the pastes as a result of the 48 hour exposure at 500 F, as shown in Table 7.

**TABLE 7**

<table>
<thead>
<tr>
<th>Cement Paste</th>
<th>Weight Percent of Total Chemically Combined Water ( (w_n) ) in Paste Lost Due to 48 Hour Heat Exposure at 500 F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>39</td>
</tr>
<tr>
<td>0.45</td>
<td>35</td>
</tr>
<tr>
<td>0.60</td>
<td>44</td>
</tr>
<tr>
<td>Paste Identification</td>
<td>As-Cured Paste</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------------</td>
</tr>
<tr>
<td></td>
<td>Evaporable Water, w_e</td>
</tr>
<tr>
<td></td>
<td>Weight %</td>
</tr>
<tr>
<td>0.33</td>
<td>13.2</td>
</tr>
<tr>
<td>0.45</td>
<td>17.7</td>
</tr>
<tr>
<td>0.60</td>
<td>22.3</td>
</tr>
</tbody>
</table>

(a) Average value of measurements on eight specimens.
(b) Average value of measurements on four specimens.
Figure 18. Effect of curing and heat exposure on water content of cement pastes.

Total Water Content of Pastes, Weight per cent

- Fresh Paste
- 70 Day Old Paste, Before Heating
- After Heating 250°F, 48 Hours
- After Heating 500°F, 48 Hours

Water Lost On Heating

0.60 PASTE
0.45 PASTE
0.33 PASTE
Effect of Heat Exposure on the Dimensional Stability of Hardened Cement Paste and Mortar

The deformation and weight loss exhibited by the cement paste and mortar specimens on heating to 500 F using the four heating schedules described previously are shown graphically in Figures 19-22 for 0.33 paste, Figures 23-26 for the 0.45 paste, Figures 27-29 for the 0.60 paste; and Figures 30-32 for the mortar. Specimen deformation is plotted as the linear dimensional change in percent (based on the original specimen length; as-cured condition, no heat exposure). The weight loss of the heated specimens is plotted as the percent of the final weight loss at the conclusion of the study. For example, a 50 percent loss at 200 F implies that for that particular heating schedule, half of the total weight lost had occurred by the time the specimen had reached 200 F. The reference state for all of the specimens shown in Figures 19-32 (i.e., the point of zero strain and zero weight loss) was the saturated specimen at room temperature.

All of the specimens heated according to the same heating schedule exhibited similar deformational behavior (i.e., the general shape of the deformation versus temperature curve was similar). However, the absolute magnitude of the deformation varied depending on the composition of the specimen. Specimens having nominally the same composition (same w/c ratio) displayed quite different deformational behavior depending on the heating schedule employed. All specimens exhibited a permanent contraction after heating to 500 F regardless of the heating schedule used. The magnitude of this
Figure 19. Effect of heat exposure on the dimensional stability of 0.33 cement paste (Heating Schedule A).
Figure 20. Effect of heat exposure on the dimensional stability of 0.33 cement paste (Heating Schedule B).
Figure 21. Effect of heat exposure on the dimensional stability of 0.33 cement paste (Heating Schedule C).
Figure 22. Effect of heat exposure on the dimensional stability of 0.33 cement paste (Heating Schedule CV).
Figure 23. Effect of heat exposure on the dimensional stability of 0.45 cement paste (Heating Schedule A).
Figure 24. Effect of heat exposure on the dimensional stability of 0.45 cement paste (Heating Schedule B).
Figure 25. Effect of heat exposure on the dimensional stability of 0.45 cement paste (Heating Schedule C).
Figure 26. Effect of heat exposure on the dimensional stability of 0.45 cement paste (Heating Schedule C^v).
Figure 27. Effect of heat exposure on the dimensional stability of 0.60 cement paste (Heating Schedule A).
Figure 28. Effect of heat exposure on the dimensional stability of 0.60 cement paste (Heating Schedule C).
Figure 29. Effect of heat exposure on the dimensional stability of 0.60 cement paste (Heating Schedule CV).
Figure 30. Effect of heat exposure on the dimensional stability of mortar (Heating Schedule A).
Figure 31. Effect of heat exposure on the dimensional stability of mortar (Heating Schedule C).
Figure 32. Effect of heat exposure on the dimensional stability of mortar (Heating Schedule C^V).
permanent contraction in specimens of the same composition was always greatest in the case of the lower heating rates (Schedule A) and the case where water removal was effected before heating commenced (Schedule Cv). This feature of the data is shown in detail in Table 8. Following their exposure at 500 F, the cement pastes exhibited normal reversible thermal expansion on reheating to 500 F.

**TABLE 8**

PERMANENT LINEAR CONTRACTION OF CEMENT PASTE AND MORTAR SPECIMENS ON HEATING TO 500 F

<table>
<thead>
<tr>
<th>Heating Schedule</th>
<th>Permanent Linear Contraction, Percent of Original Specimen Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.33 Paste</td>
</tr>
<tr>
<td>A</td>
<td>1.27</td>
</tr>
<tr>
<td>B</td>
<td>0.88</td>
</tr>
<tr>
<td>C</td>
<td>0.87</td>
</tr>
<tr>
<td>Cv</td>
<td>1.01</td>
</tr>
</tbody>
</table>

The Loss of Water From Heated Pastes.—The total weight loss exhibited by the pastes on heating to 500 F consisted of losses of both evaporable water \( (w_e) \) and nonevaporable water \( (w_n) \). Further distinction can be made on the basis of the fact that the evaporable water can be broken down into two components, viz., water in the capillary pores \( (w_c) \) and water in the gel pores \( (w_g) \). Thus, the total weight loss \( (\Delta w_t) \) experienced by the pastes on heating to 500 F can be
expressed as:

\[ w_t = w_g + w_c + w_n \]  \hspace{1cm} (1)

The results presented in Table 2 and 6 permit a calculation to be made of the relative contributions of \( w_g \), \( w_c \), and \( w_n \) to the measured \( \Delta w_t \) for all the pastes studied. A sample calculation for the 0.33 pastes is given below:

Total water lost on heating to 500 F, percent of the original paste weight is:

\[ \Delta w_t/m = 0.177 \]

Total evaporable water lost on heating to 500 F, percent of the original paste weight, is:

\[ w_e/m = 0.132 \]

Total nonevaporable water lost on heating to 500 F, percent of the original paste weight, is:

\[ w_n/m = 0.045 \]

Of the evaporable water lost, it was shown previously that for the 0.33 pastes, 65.6 percent of this water was gel water and 34.4 percent was capillary water. Thus, it is possible to express the evaporable water loss as:

\[ 0.656 \times 0.132 = 0.0865 = w_g/m \]

\[ 0.344 \times 0.132 = 0.0455 = w_c/m \]
The total weight lost on heating the 0.33 paste to 500 F is expressed as:

$$\Delta w_{t/m} = \frac{w_c}{m} + \frac{w_g}{m} + \frac{w_n}{m} \quad (2)$$

$$(0.177) = (0.0455) + (0.0865) + (0.045)$$

It is desirable to express equation (2) explicitly in terms of the percent of the total weight loss represented by each of the three types of water. Dividing each term in equation (2) by $\Delta w_{t/m}$ yields:

$$1.0 = 0.257 + 0.489 + 0.254$$

$$(w_t) \quad (w_c) \quad (w_g) \quad (w_n)$$

Of the total amount of water removed from the 0.33 pastes on heating to 500 F, 25.7 percent was evaporable water present in the capillary porosity of the paste, 48.9 percent was evaporable water contained in the gel pores of the paste; and 25.4 percent was chemically combined water. From considerations discussed previously, it can be assumed that on initial heating of a saturated paste the capillary water will be the first to exit, followed by the gel water; and finally at higher temperatures (>250 F) a portion of the chemically combined water will be lost. On this basis, in Figures 19 through 22 the first 25.7 percent of the weight loss is due to the removal of all of the capillary water, and the next 48.9 percent is due to the removal of all the gel water. All of the evaporable water has been removed from the paste when 74.6 percent of the total weight loss has occurred. The final 25.4 percent of weight loss is due to the removal of nonevaporable
(chemically combined water) from the pastes.

In a similar manner it can be shown for the 0.45 pastes that:

\[ 1.0 = 0.33 + 0.42 + 0.25 \]
\[ (w_t) \quad (w_c) \quad (w_g) \quad (w_n) \]

so that all the evaporable water is removed when 75 percent of the water has been removed.

For the 0.60 pastes:

\[ 1.0 = 0.426 + 0.374 + 0.200 \]
\[ (w_t) \quad (w_c) \quad (w_g) \quad (w_n) \]

so that the paste is void of evaporable water when 80 percent of the water has been removed.

These results are summarized in Table 9. Due to the somewhat

**TABLE 9**

*THE LOSS OF WATER FROM CEMENT PASTES ON HEATING TO 500 F*

<table>
<thead>
<tr>
<th>Cement Paste Identification</th>
<th>Percent of the Total Water Lost From Cement Paste on Heating to 500 F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Capillary Water (w_c)</td>
</tr>
<tr>
<td>0.33</td>
<td>25.7</td>
</tr>
<tr>
<td>0.45</td>
<td>33.0</td>
</tr>
<tr>
<td>0.60</td>
<td>42.6</td>
</tr>
</tbody>
</table>
arbitrary definitions of $w_c$, $w_g$, and $w_n$, and to nonequilibrium conditions during heating, the figures quoted in Table 9 cannot be taken strictly literally. However, they may be expected to represent a reasonable approximation of the actual situation.

**Paste Deformation During Water Removal.**—The data shown in Figures 19 through 32 show that all the pastes underwent contraction during heating when both evaporable and nonevaporable water was being lost. Close scrutiny of the raw data, however, suggested that once the evaporable water had been removed from the pastes, their deformational behavior on further heating was quite similar, i.e., the deformation accompanying the removal of the chemically combined water (nonevaporable) from the pastes appeared to be relatively independent of heating rate and specimen composition. To determine whether this was the case calculations were made of the total contractive deformation experienced by the pastes during the period of time in which only nonevaporable water was being lost. The fact that different heating rates were used, however, meant that the temperature of the paste at the time all the evaporable water was removed varied depending on which heating schedule was employed. For example, most of the evaporable water was removed from the $C^v$ series specimens before they were heated at all, while the $C$ series samples reached well over 300 F before all the evaporable water was removed. For this reason, the expansive strain due to thermal expansion of the paste had to be considered in the calculations. The contractive deformation accompanying the removal of nonevaporable water from the pastes, $C_w$, was determined
from the relationship,

\[ \varepsilon_{wn} = \left[ \frac{\Delta L}{L_0} \right]_{wn} - \left[ \frac{\Delta L}{L_0} \right]_{we} + \alpha \Delta T \]  

(3)

where

\[ \left[ \frac{\Delta L}{L_0} \right]_{wn}^{*} \]

is the measured linear deformation of the paste at the point during heating where all of the evaporable water had been removed; expressed in percent.

\[ \left[ \frac{\Delta L}{L_0} \right]_{wn} \]

is the measured linear deformation of the paste at any point after all the evaporable water has been removed during heating, i.e., the measured deformation during the period of nonevaporable water loss from the paste, expressed in percent.

\[ \Delta T \]

is the difference in the temperature of the specimen at the point during heating where all the evaporable water has been removed and the temperature of the specimen during subsequent heating, i.e., the temperature of the paste when \[ \left[ \frac{\Delta L}{L_0} \right]_{wn} \] was recorded minus the temperature of the paste when \[ \left[ \frac{\Delta L}{L_0} \right]_{we}^{*} \] was recorded; expressed in °F.

\[ \alpha \]

is the coefficient of linear thermal expansion of cement paste containing no evaporable water and was calculated from deformation data obtained on cooling the heated pastes from 500 F down to 75 F; expressed as percent per °F.

An example of the calculations involved in determining \( \varepsilon_{wn} \) as a function of the loss of \( w_n \) from heated paste is shown in Table 10. Identical calculations were made for all of the 0.33, 0.45, and 0.60
## TABLE 10
Calculation of Cement Paste Contraction Accompanying the Removal of Nonevaporable Water During Heating

Specimen 4-4-1, \( a = 5.88 \times 10^{-4} \) (Percent/F)

Temperature of Paste at Point Where All Evaluation Water is Gone - 252 F

\[
\frac{\Delta L}{L_0} = 0.185 \text{ percent}
\]

<table>
<thead>
<tr>
<th>Time From Start of Loss of ( w_n ), hrs.</th>
<th>Temp., ( ^\circ F )</th>
<th>( \Delta T )</th>
<th>( \Delta T \times a )</th>
<th>Linear Deformation of Paste During the Loss of ( w_n ), Percent</th>
<th>Calculated Deformation of Paste Due to Loss of ( w_n ), Percent</th>
<th>Water Loss</th>
<th>Percent of Non-Evaporable Total Water Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>252</td>
<td>0</td>
<td>0</td>
<td>.185</td>
<td>0</td>
<td>75.0</td>
<td>0</td>
</tr>
<tr>
<td>.3</td>
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<td>&quot;</td>
<td>&quot;</td>
<td>.191</td>
<td>.006</td>
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<td>6.0</td>
</tr>
<tr>
<td>.5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
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<td>.017</td>
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<td>19.6</td>
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<tr>
<td>1.2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>.269</td>
<td>.084</td>
<td>80.5</td>
<td>22.0</td>
</tr>
<tr>
<td>2.1</td>
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<td>&quot;</td>
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<td>.326</td>
<td>.141</td>
<td>82.4</td>
<td>29.6</td>
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<tr>
<td>5.0</td>
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<td>&quot;</td>
<td>&quot;</td>
<td>.397</td>
<td>.212</td>
<td>84.0</td>
<td>36.0</td>
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<tr>
<td>20.0</td>
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<td>&quot;</td>
<td>&quot;</td>
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<td>.265</td>
<td>85.5</td>
<td>42.0</td>
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<tr>
<td>20.5</td>
<td>331</td>
<td>.79</td>
<td>.046</td>
<td>.399</td>
<td>.260</td>
<td>86.4</td>
<td>45.6</td>
</tr>
<tr>
<td>20.7</td>
<td>353</td>
<td>101</td>
<td>.059</td>
<td>.377</td>
<td>.251</td>
<td>86.9</td>
<td>47.6</td>
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<tr>
<td>20.9</td>
<td>370</td>
<td>118</td>
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<tr>
<td>21.0</td>
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<td>89.6</td>
<td>58.4</td>
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<td>406</td>
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<td>90.7</td>
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<tr>
<td>21.3</td>
<td>424</td>
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<td>.433</td>
<td>.349</td>
<td>92.0</td>
<td>68.0</td>
</tr>
<tr>
<td>21.5</td>
<td>443</td>
<td>191</td>
<td>.112</td>
<td>.486</td>
<td>.413</td>
<td>93.5</td>
<td>74.0</td>
</tr>
<tr>
<td>21.7</td>
<td>462</td>
<td>210</td>
<td>.123</td>
<td>.510</td>
<td>.448</td>
<td>94.9</td>
<td>79.6</td>
</tr>
<tr>
<td>22.0</td>
<td>480</td>
<td>228</td>
<td>.134</td>
<td>.558</td>
<td>.507</td>
<td>95.9</td>
<td>83.6</td>
</tr>
<tr>
<td>22.1</td>
<td>492</td>
<td>240</td>
<td>.141</td>
<td>.589</td>
<td>.545</td>
<td>96.7</td>
<td>86.8</td>
</tr>
<tr>
<td>22.3</td>
<td>499</td>
<td>247</td>
<td>.145</td>
<td>.651</td>
<td>.611</td>
<td>97.4</td>
<td>89.6</td>
</tr>
<tr>
<td>22.9</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>.698</td>
<td>.658</td>
<td>97.9</td>
<td>91.6</td>
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<tr>
<td>23.7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>.725</td>
<td>.685</td>
<td>98.7</td>
<td>94.8</td>
</tr>
<tr>
<td>26.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>.806</td>
<td>.766</td>
<td>99.2</td>
<td>96.8</td>
</tr>
<tr>
<td>30.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>.852</td>
<td>.812</td>
<td>99.7</td>
<td>98.8</td>
</tr>
<tr>
<td>45.0</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>.939</td>
<td>.899</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Figure 33. Contraction of heated cement pastes accompanying loss of nonevaporable water.
used in the study* (shown in Figures 19 through 29). These data are presented in Figure 33 which shows the contraction of the cement pastes accompanying the loss of nonevaporable water \[ \epsilon_{wn} \] as a function of the percent of the total nonevaporable water lost from the pastes on heating to 500 F. Close examination of the data points suggested that the data can be expressed as two linear plots with a break coming after about 80 percent of the \( w_n \) had been lost. Simple linear regression analyses were performed using the data points shown in Figure 33 and gave the following best fit curves for the two linear portions of the relationship. Between 0 and 80 percent loss of the \( w_n \),

\[
\epsilon_{wn}(0-80) = 0.015 + 0.622 w_n
\]

The estimation of the standard deviation for this equation was,

\[
s_{y|x} = 0.081 \text{ percent}
\]

Between 80 and 100 percent loss of the \( w_n \),

\[
\epsilon_{wn}(80-100) = -1.076 + 1.997 w_n
\]

The estimation of the standard deviation for this equation was,

\[
s_{y|x} = 0.108 \text{ percent}
\]

The total contractive deformation accompanying the loss of \( w_n \),

*Except for the 0.33 pastes heated according to C, C', and B. These were omitted from this calculation inasmuch as their actual heating schedule differed somewhat from that of the other pastes.
on heating 0.33, 0.45, and 0.60 pastes to 500 F using the indicated heating schedules was determined as (95 percent confidence interval),

\[ \varepsilon^{*}_{wn} = -0.944 \pm 0.088 \]

It is indicated that about half of \( \varepsilon^{*}_{wn} \) occurs during the loss of the first 80 percent of \( wn \) and half during the loss of the remaining 20 percent of \( wn \). If it can be assumed that the contraction of the heated pastes due to the loss of nonevaporable water is independent of paste composition and heating rate, then this suggests that the significant differences in permanent contraction of pastes having the same composition are controlled primarily by the manner of removal of evaporable water from the pastes. Consider, for example, the data on the 0.45 pastes shown in Figures 25 and 26. These specimens were the same composition and were subjected to the same heating schedule. The only difference in these two tests was that one specimen (Figure 26) was subjected to vacuum drying at room temperature so that most of the evaporable water had been removed prior to any heating. The contraction of this specimen at the point where all the evaporable water was removed (275 F) was 0.55 percent. By contrast, the contraction of the specimen heated from the saturated state at the same rate (Figure 25) at the point where all the evaporable water was removed (345 F) was 0.05 percent. Clearly, the interplay between the evaporable water content and temperature of the pastes had a marked effect on their deformation during heating. A similar phenomenon was observed with the 0.60 paste (Figures 28 and 29) and with the 0.33 paste.
(Figures 21 and 22).

The manifestation, if not the mechanism of this interplay, was elucidated somewhat by a not too obvious relationship that was shown to exist between the final permanent contraction of the paste specimens on cooling to room temperature \( \varepsilon_{\text{tot}} \) and the factors known to influence this parameter, viz., thermal expansion, deformation occurring during the loss of nonevaporable water, and the deformation occurring during the loss of evaporable water. It was deduced, for the pastes studied, that:

\[
\varepsilon_{\text{tot}} = \left[ \frac{\Delta L}{L_0} \right]_{w_n}^* + \varepsilon_{w_n}^* + \alpha \Delta T \tag{4}
\]

where,

- \( \varepsilon_{\text{tot}} \) is the permanent contraction of the heated paste specimens measured at room temperature, percent of original specimen length.
- \( \left[ \frac{\Delta L}{L_0} \right]_{w_n}^* \) has the same meaning as in equation (3) and is a unique value in each paste studied.
- \( \varepsilon_{w_n}^* \) is the total contractive deformation exhibited by the pastes during the loss of nonevaporable water, i.e., the value of \( w_n \) of equation (3) at the point where \( w_n = 100 \), percent of original specimen length.
- \( \alpha \) has the same meaning as in equation (3).
- \( \Delta T \) in this case is the temperature difference between the temperature of the paste at the point corresponding to complete removal of the evaporable water and the temperature of the paste at which the permanent contraction, \( \varepsilon_{\text{tot}} \), is measured, i.e., room temperature, 75 F.
As an example, consider the 0.60 paste heated according to Schedule C (Figure 28). For this specimen the evaporable water is completely removed when 80 percent of the total water lost has been removed, i.e., at 352 F. At that point the specimen contraction, $\frac{\Delta L}{L_0}$, is 0.12 percent. The expansion of the specimen at 352 F due solely to the effects of thermal expansion is $\alpha \Delta T$ or $(6.55 \times 10^{-4}) (352-75) = 0.18$ percent. It is seen that this value must be added to $\frac{\Delta L}{L_0}$ to obtain the actual specimen contraction due to the loss of evaporable water at 352 F. The measured value of $\epsilon_{w_n}$ for this specimen was 0.81 percent so that the calculated value of the permanent contraction of this specimen at room temperature is from equation (4), $\epsilon_{tot} = 0.12 + 0.80 + 0.18 = 1.10$ percent.

The actual permanent contraction as measured in the experiment was 1.11 percent. The permanent contraction $[\epsilon_{tot}]$ of all the paste specimens examined in the study was calculated from equation (4) using the procedure just described. These calculated data are shown in Table 11 along with the measured value of permanent contraction. The good agreement between the calculated and measured values is obvious. Although the measured values of $\epsilon_{w_n}$ for each specimen were used in the calculations of Table 11, it is obvious that the use of the calculated value of $\epsilon_{w_n}$, viz., 0.944±0.088 percent, could have been used to establish the usefulness of equation (4), albeit with some sacrifice in the correlation of the calculated and measured values of $\epsilon_{tot}$. In any event it is seen that with prior knowledge of $\epsilon_{w_n}$ and $\alpha$, it is
only necessary to determine \( \left( \frac{AL}{L_0} \right)_{we}^\star \), and the corresponding temperature at the time \( \left( \frac{AL}{L_0} \right)_{we}^\star \) is recorded to be able to predict the final permanent contraction of any paste specimen heated to 500 °F.

### TABLE 11

**MEASURED AND CALCULATED VALUES OF THE PERMANENT CONTRACTION OF HEATED CEMENT PASTE SPECIMENS**

\[
\varepsilon_{tot} = \left( \frac{AL}{L_0} \right)_{we}^\star + \varepsilon_{w_n}^\star + \alpha A T
\]

<table>
<thead>
<tr>
<th>Specimen Identification, Heating Schedule</th>
<th>( \left( \frac{AL}{L_0} \right)_{we}^\star )</th>
<th>( \varepsilon_{w_n}^\star )</th>
<th>( \alpha A T )</th>
<th>Permanent Contraction</th>
<th>Measured</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-31 (C)</td>
<td>0.12</td>
<td>0.80</td>
<td>0.18</td>
<td>1.10</td>
<td>1.11</td>
<td></td>
</tr>
<tr>
<td>6-32 (A)</td>
<td>0.52</td>
<td>0.98</td>
<td>0.07</td>
<td>1.57</td>
<td>1.59</td>
<td></td>
</tr>
<tr>
<td>6-33 (CV)</td>
<td>0.78</td>
<td>1.01</td>
<td>0.21</td>
<td>2.00</td>
<td>1.99</td>
<td></td>
</tr>
<tr>
<td>4-4-1 (B)</td>
<td>0.18</td>
<td>0.90</td>
<td>0.11</td>
<td>1.19</td>
<td>1.18</td>
<td></td>
</tr>
<tr>
<td>4-4-2 (CV)</td>
<td>0.55</td>
<td>1.09</td>
<td>0.13</td>
<td>1.77</td>
<td>1.78</td>
<td></td>
</tr>
<tr>
<td>4-4-3 (A)</td>
<td>0.38</td>
<td>1.06</td>
<td>0.08</td>
<td>1.52</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>4-2-1 (C)</td>
<td>0.05</td>
<td>0.88</td>
<td>0.17</td>
<td>1.10</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>D-3 (A)</td>
<td>0.33</td>
<td>0.84</td>
<td>0.11</td>
<td>1.28</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>C-3 (CV)</td>
<td>0.18</td>
<td>0.67</td>
<td>0.17</td>
<td>1.02</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>C-4 (B)</td>
<td>0.12</td>
<td>0.66</td>
<td>0.11</td>
<td>0.89</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td>C-2 (C)</td>
<td>0.08</td>
<td>0.58</td>
<td>0.17</td>
<td>0.83</td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>
Behavior of Mortar During Heating.—The deformational behavior of the mortar specimens on heating to 500 F by the various heating schedules is shown in Figures 30-32. The overall effect of replacing 50 volume percent of the 0.45 paste with an elastic solid dispersed phase was to greatly diminish the contraction of the paste matrix phase on heating. This is clearly seen in the data in Table 12 comparing the permanent contraction of the mortar specimens (which contained 0.45 paste) with that of the 0.45 paste specimens for the various heating schedules.

**TABLE 12**

<table>
<thead>
<tr>
<th>Heating Schedule</th>
<th>Permanent Contraction of Mortar Specimen, $\varepsilon_{\text{tot}}$ (mortar) percent</th>
<th>Permanent Contraction of 0.45 Paste Specimens, $\varepsilon_{\text{tot}}$ (0.45 paste) percent</th>
<th>$\varepsilon_{\text{tot}}$ (mortar) percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.20</td>
<td>1.52</td>
<td>13.2</td>
</tr>
<tr>
<td>C</td>
<td>0.18</td>
<td>1.10</td>
<td>16.3</td>
</tr>
<tr>
<td>$CV$</td>
<td>0.28</td>
<td>1.78</td>
<td>15.7</td>
</tr>
</tbody>
</table>

For any given heating schedule the permanent contraction of the mortar was only about 15 percent that of the pure paste specimen. However, the influence of the cement paste in controlling the magnitude of the permanent contraction of the mortar specimens is again obvious, i.e., greater contraction was effected if the evaporable water was removed prior to heating (Schedule $CV$) relative to heating rapidly from
saturation (Schedule C). The mortar specimen heated according to Schedule C showed only 65 percent of the contraction of the specimen heated according to Schedule CV (0.18/0.28 = 0.65). This observation was also true for the pure 0.45 paste specimens (1.10/1.78 = 0.62). It is seen also that the contraction of the mortar specimen during vacuum drying at room temperature (0.125 percent) was only about 18 percent that experienced by the pure 0.45 paste specimen during the same treatment (0.70 percent).

The contractive deformation accompanying the loss of non-evaporable water from the heated mortar specimens ($\varepsilon_{w_n}$) on heating to 500 F was calculated using equation (3) and the procedure described previously for the paste specimens, and is presented in Figure 34. These data (Figure 34) may be compared to Figure 33 which shows $\varepsilon_{w_n}$ versus $w_n$ for the pure 0.45 pastes. The effect of the dispersed quartz phase was to reduce the magnitude of $\varepsilon_{w_n}$ of the mortar at any given value of $w_n$ by about one order of magnitude relative to the pure paste specimens. The overall influence of $w_n$ on $\varepsilon_{w_n}$ for the mortar was, however, similar to that exhibited by the pure paste specimens. Between 0 and about 95 percent of the total loss of $w_n$ the best fit line expressing the relationship was:

$$\varepsilon_{w_n} = 0.008 + 0.054 w_n$$

The estimate of the standard deviation for this equation was:

$$s_{y|x} = 0.011 \text{ percent}$$

The best fit line representing $\varepsilon_{w_n}$ versus $w_n$ for $w_n$ loss from 95 to 100 percent was:
Contractive Deformation Accompanying Loss of Nonevaporable Water From Heated Pastes ($e_{wn}$), Per cent of original specimen length

Figure 34. Contraction of heated mortar accompanying loss of nonevaporable water.
\[ \varepsilon_{wn} = -0.556 + 0.650w_n, \]

with a standard deviation of:

\[ \sigma_{\varepsilon|\varepsilon} = 0.018 \text{ percent}. \]

Sintering Studies

The indicated complex relationship between \( \varepsilon_{we} \) and the variables time, temperature, and \( w_e \), and the unique behavior of \( \varepsilon_{wn} \) as influenced by \( w_n \) made it desirable to study in greater detail the effect of temperature, per se, on the contraction and general behavior during heating of cement paste. This was accomplished through studies on compacts prepared from hydrated portland cement that had been heated to 500 F prior to compaction. The starting material in these compacts, prepared as a powder, was hydrated portland cement that was void of evaporable water and with a loss of chemically combined water comparable to the paste specimens used in the studies just discussed. The effect of further exposure to elevated temperatures up to 500 F on the dimensional stability and strength of the compacts was then studied.

A cement-water slurry (2,000 gms. cement/3,000 gms. water) was ball-milled for 60 hours in a gallon size ball mill using cylindrical grinding pebbles. The cement was the Type I cement used in all the previous work. The purpose of the milling procedure and the high water/cement ratio was to produce a paste with a high maturity factor. After milling, the nonevaporable water content \( (w_n/c) \), of the paste was measured and determined to be 0.203 (a maturity factor of about 0.78). The paste slurry was then poured into suitable containers and slowly heated to 500 F where it was held for 48 hours. After firing
the paste was crushed to -80 mesh powder and stored in a moisture-free environment. Four series of five cylindrical compacts (-1/4 inches in diameter and 1.0 inches in length and weighing ~18 grams) were then prepared from this powder as follows: Series A, B, and C were compacted at room temperature at 1700 psi. Series D was warm-pressed at 500 F and 1700 psi in the same die and press as Series A, B, and C. Series A and D samples were placed in dessicators immediately after pressing. Series B samples were heated to 500 F and held for 20 hours. Series C samples were heated to 500 F and held for 9 days before cooling and storing in a dessicator.

The compressive strength of the compacts from all four series was then determined. Data regarding the shrinkage during heat exposure and the compressive strength of all the compacts are presented in Table 13. A significant contractive deformation occurred in the Series B and C compacts following their exposure to 500 F for 20 hours and 9 days, respectively. Inasmuch as no evaporable or nonevaporable water was lost from these compacts during heating, it may be surmised that the contraction exhibited by these compacts was related solely to the effects of the elevated temperature.

The effect of heat exposure (to 500 F) was to increase the compressive strength of the compacts pressed at room temperature by about 25 percent. The strength of the specimens compacted at 500 F exceeded the strength of compacts pressed at room temperature by 115 percent.
TABLE 13
STRENGTH AND SHRINKAGE OF HYDRATED CEMENT COMPACTS

<table>
<thead>
<tr>
<th>Series</th>
<th>Compressive Strength (a) After Indicated Treatment, psi</th>
<th>Linear Shrinkage (b) After Indicated Treatment, Percent of Original Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td>193.4±14.2</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>Compacted at room temperature. No further treatment.</td>
<td></td>
</tr>
<tr>
<td>B.</td>
<td>240.4±12.1</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Compacted at room temperature, then heated 20 hours at 500 F.</td>
<td></td>
</tr>
<tr>
<td>C.</td>
<td>244.0±18.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Compacted at room temperature, then heated 9 days at 500 F.</td>
<td></td>
</tr>
<tr>
<td>D.</td>
<td>416.0±81.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Warm pressed at 500 F.</td>
<td></td>
</tr>
</tbody>
</table>

(a) Average of values measured on 5 specimens, 95 percent C.I.
(b) Average of values measured on 5 specimens.

Discussion of Experimental Results

The results of the present study indicate that as many as four sources of deformation contribute to the dimensional instability of unstressed portland cement paste heated at temperatures up to 500 F, viz.,

1. Thermal expansion.
2. Contraction accompanying the removal of nonevaporable water.
3. Contraction accompanying the removal of evaporable water.
4. Autogenous contraction due to a sintering phenomenon.
The contractive deformation sources dominate the deformation behavior of heated pastes as evidenced by the fact that all of the pastes studied exhibited a permanent contraction after heating to 500 F. The magnitude of the permanent contraction of heated pastes, \( \varepsilon_{\text{tot}} \), was correlated to environmental and body parameters through the empirical relationship,

\[
\varepsilon_{\text{tot}} = \left[ \frac{\Delta L}{L_0} \right]_{w_e}^* + \varepsilon_{w_n}^* + \alpha \Delta T \quad (4)
\]

Inasmuch as \( \varepsilon_{w_n} \) and \( \alpha \) may be considered to be constants for the cement used in this study, it may be concluded that the magnitude of the permanent contraction in heated pastes is directly controlled by the manner in which evaporable water is removed from the paste relative to its heating history, i.e., by the variables controlling the magnitude of \( \left[ \frac{\Delta L}{L_0} \right]_{w_e}^* \), viz., time, temperature, evaporable water content, and specimen geometry.

The Removal of Evaporable Water From Heated Cement Paste As Related to Paste Deformation

From a mechanistic point of view the contractive deformation associated with the removal of evaporable water from heated cement pastes may be considered as analogous to drying shrinkage, i.e., the isothermal contraction associated with the loss of evaporable water from pastes at normal ambient temperature. Previous studies of drying shrinkage\(^{51}\) and of creep\(^{49}\) during drying in cement pastes at room temperature have led to the postulation that considerable structural
rearrangement of the colloidal gel crystallites takes place as evaporable water is being lost from the paste. The overall result of this structural rearrangement in cement pastes during normal drying is that solid gel surfaces are closer together in the dried paste than they were in the saturated paste. In instances where the approach of the gel surfaces has been optimum from the standpoint of proximity and mutual contact area solid-solid bonding can develop. Enough of this bonding occurs so that about 20 percent of the shrinkage that takes place in cement paste during normal drying is permanent and has been termed irreversible shrinkage. Mills has presented electron micrographs showing visual evidence of the collapse of hydrated cement gel during dehydration. It was suggested by this investigator that the phenomenon depicted was probably not unlike the phenomenon occurring in pastes dried for the first time. Profound changes in structure were visualized during the first desorbing cycle. The contractive deformation of concrete under a compressive stress at normal temperatures is greatly increased if the concrete is simultaneously undergoing a loss of evaporable water, i.e., is being dried. The deformation of dry or saturated concrete under stress, on the other hand, is considerably less. The increased deformation of concrete under stress during drying is viewed as a consolidation of gel particles into spaces previously occupied by water with the establishment of point to point solid particle contact.

From these and other studies comes the picture that the cement gel phase is exceedingly mobile during the time in which evaporable
water is being removed during first-time drying. It is conceivable that during drying the individual gel crystallites are continually changing their position relative to the remainder of the gel with the freedom of motion dictated to some extent by the degree of bonding with other solid elements of the gel (either solid-solid bonding or through a mutually shared adsorbed water layer). It is envisioned that the movement of the gel crystallites in response to strain accompanying the removal of evaporable water is facilitated by the presence of adsorbed water layers on their surface. As the last vestiges of evaporable water leave the paste, the mobility of the gel is sharply curtailed since the bonds between gel crystallites are predominantly solid-solid and no adsorbed water layers remain to act as lubricants between two solid gel surfaces in close proximity. This picture of the mobility of cement gel during drying is fortified by the results of studies of creep in concrete or cement paste that is simultaneously drying. In this case the gel particles can also move in response to an externally applied stress; in the simplest sense, if the stress is compressive, the process may be viewed to operate much as a powder is compacted in a die. The external stress produces a closer approach of gel crystallites than would occur if drying shrinkage were operating alone. This event is manifested as an increase in the amount, and perhaps degree of solid-solid bonding, as evidenced on a macro-scale by an increase in the strength of the paste. As might be expected, the amount of irreversible creep exceeds the amount of irreversible shrinkage.
Whereas a compressive stress acts to densify a paste that is undergoing drying, a tensile force acting on the paste at this time would tend to pull the paste apart, i.e., an expansive deformation would occur. In this vein it is suggested that the application of any compressive stress regardless of its origin (thermal stress, aggregate restraint) to cement paste during drying will deform the cement gel in such a way as to enhance the close contact of the gel surfaces. The opposite effect would result if a tensile stress regardless of its origin is imposed on the paste during its period of drying.

The deformational behavior of the cement pastes in the present study during heating in the time where evaporable water is being lost is amenable to explanation in terms of a highly mobile cement gel phase that is deforming in response to outside sources of stress. During first heating of cement paste continuous rearrangement of the gel crystallites occurs as evaporable water is lost from the paste, resulting in a contraction in the paste. The thermal expansion is viewed as a potential source of tensile stress which tends to elongate or dilate the gel. If heating is rapid, evaporable water contained in the paste, unable to exit quickly enough, will increase in volume in situ. Such an event would actually increase the distance between the solid surfaces in mutual contact with this water—an expansion which would be superimposed on the normal thermal expansion of the solid phases. That such an event actually does take place is suggested by the observed abnormally high initial expansions of rapidly heated paste specimens in the present study. Reference to Figure 22 can illustrate this point.
For this dense 0.33 paste the five day vacuum drying period prior to heating removed only about 75 percent of the total evaporable water in the paste. The paste was then heated rapidly to 500 F. An abnormally high expansion was exhibited by the paste on heating from room temperature up to about 200 F. During this time, due to the rapid heating rate, almost no evaporable water was removed from the specimen. The actual room temperature to 200 F coefficient of linear thermal expansion for this specimen was $10.4 \times 10^{-4}$ as compared to the coefficient of the same paste free of evaporable water of $6.6 \times 10^{-4}$. This behavior was not exhibited by the 0.45 and 0.60 pastes heated according to the same schedule $[CV]$. However, for these less dense pastes the five day vacuum drying period was sufficient to remove most or all of the evaporable water. (See Figures 26 and 29.) It is indicated that if saturated pastes are rapidly heated, the expansion of the solid phases combined with the expansion of the evaporable water remaining in the paste, in effect, acts to pull apart the still highly mobile gel; and the result on a macroscale is an expansion of the paste even though some evaporable water is being lost. This expansion continues until the rate of evaporable water removal is increased to the point where the contraction accompanying the loss of evaporable water can exceed the thermal expansion. Indeed, the rate of contraction of the rapidly heated pastes (Schedule C) during the time evaporable water was being lost increased in direct proportion to the increase in the rate of water loss from the paste during this time. The actual contraction of the pastes heated rapidly in the saturated
state at the point in time when all their evaporable water had been removed was only a fraction of the contraction that would have occurred if the evaporable water had been removed at room temperature. Other workers have observed this same phenomenon. Mills observed that the linear shrinkage of a paste specimen vacuum dried for fifteen months was double that of a companion specimen heated at 110°C for seven days.

The deformation of a heated paste relative to its original dimension at the time the last of the evaporable water is driven off is of paramount importance, for beyond this point the cement paste may no longer be considered mobile. The microstructure of the paste at that point is fixed by the predominance of solid-solid bonding. The geometry of the paste at this point may be either one of expansion or contraction relative to the original geometry of the paste depending on the forces influencing the movement of the paste during the loss of evaporable water. Unless all the factors that influence the deformation of the paste during the loss of \( w_e \) can be identified and measured, the final deformation of the paste at the moment when all free water has been removed cannot be predicted.

The Removal of Nonevaporable Water from Heated Cement Paste as Related to Paste Deformation

The contractive deformation accompanying the removal of chemically combined water from cement paste on heating is viewed as being analogous to the contractive deformation exhibited by certain clay minerals on the loss of interlayer chemical water, i.e., the
deformation observed macroscopically is due to microscopic contractions of the crystal lattice of the material. Viewed in this manner, the deformation of the cement pastes during the loss of chemically combined water should be relatively independent of paste porosity, as was claimed based on the data shown in Figure 33. By the same token, however, there is reason to suspect that paste deformation due to the loss of nonevaporable water should be a reasonably linear function of the nonevaporable water content. Obviously this was not the case as reference to Figure 33 quickly shows. A plausible explanation for the observed deformational behavior of the heated pastes during the expulsion of chemically combined water is found after considerations are given to the expected effect of time, temperature, and the postulated sintering phenomenon on paste contraction.

Reference to the original data shows that the point of the change in slope of the plot of $\varepsilon_{wn}$ versus $wn$ occurs for all of the specimens at approximately the point where the 500 F maximum temperature in all the heating schedules was reached. Thus, all deformation data representing from 80 to 100 percent loss of $wn$ were obtained under isothermal conditions (500 F) and represent soak times of anywhere from 24 to 48 hours depending on the heating schedule. Deformation data taken over the $wn$ range 0 to 80 represent periods of dynamic heating (at temperatures from 200 F to 500 F) and shorter times at temperature (less than 2 hours for the pastes heated according to Schedules C and CV, 20 hours for the Schedule A specimens, and about 4 hours for the Schedule B specimens). Assume for the present that a
sintering process is operative over the entire temperature range of the study (75–500°F). Based on a knowledge of conventional sintering processes it may be assumed that the rate of sintering will increase with increased temperature and the amount of sintering will increase with time at any given temperature. It is expected that, all other things being equal, the specimen deformation, $\varepsilon_{wn}$, corresponding to a given $wn$ loss should be greater in slowly heated pastes (Schedule A) due to the fact that in the period where $wn$ was being removed these specimens were actually at temperature longer; hence contraction due to the proposed sintering mechanism should be greater. Pastes heated rapidly when $wn$ is being lost (Schedule C and CV) would be expected to exhibit less contraction due to the sintering process in view of the much shorter times at temperature.

Data are presented in Table 14 which show the values of $\varepsilon_{wn}$ after 25, 50, 75; and 100 percent of the total nonevaporable water has been expelled as influenced by the heating schedule. It is apparent that increased time at temperature correlates with increased values of $\varepsilon_{wn}$.

Inasmuch as the contractive deformation in heated pastes due to the proposed sintering mechanism is a function of time and temperature, it is to be expected that the closer to equilibrium heating conditions are the less obvious will be the break in slope of the plot of $\varepsilon_{wn}$ versus $wn$. It is apparent in Figure 33 that the slowly heated pastes (Schedule A) show less of a sharp break than pastes heated rapidly (Schedule C and CV).
TABLE 14

EFFECT OF HEATING SCHEDULE ON THE RELATIONSHIP BETWEEN $\varepsilon_{w_n}$ AND $w_n$

<table>
<thead>
<tr>
<th></th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$w_n$ Time, hr</td>
<td>$w_n$ Time, hr</td>
<td>$w_n$ Time, hr</td>
<td>$w_n$ Time, hr</td>
</tr>
<tr>
<td>Specimens heated per Schedule C and CV</td>
<td>0.07 0.1</td>
<td>0.19 0.35</td>
<td>0.39 1.1</td>
<td>0.88 46</td>
</tr>
<tr>
<td></td>
<td>0.10 0.1</td>
<td>0.28 0.35</td>
<td>0.48 1.1</td>
<td>1.09 46</td>
</tr>
<tr>
<td></td>
<td>0.10 0.1</td>
<td>0.24 0.35</td>
<td>0.47 1.1</td>
<td>1.01 46</td>
</tr>
<tr>
<td></td>
<td>0.05 0.1</td>
<td>0.13 0.35</td>
<td>0.29 1.1</td>
<td>0.81 46</td>
</tr>
<tr>
<td>Specimens heated per Schedule A</td>
<td>0.19 6.5</td>
<td>0.40 26</td>
<td>0.62 27.5</td>
<td>1.06 46</td>
</tr>
<tr>
<td></td>
<td>0.17 6.5</td>
<td>0.35 26</td>
<td>0.54 27.5</td>
<td>0.98 46</td>
</tr>
<tr>
<td></td>
<td>0.17 6.5</td>
<td>0.31 26</td>
<td>0.50 27.5</td>
<td>0.84 46</td>
</tr>
<tr>
<td>Specimens heated per Schedule B</td>
<td>0.08 1.25</td>
<td>0.28 21</td>
<td>0.41 21.5</td>
<td>0.90 45</td>
</tr>
</tbody>
</table>

It is proposed then that the contractive deformation exhibited by the heated cement pastes during the period of expulsion of non-evaporable water, as depicted in Figure 33, actually represents the contributions of two separate sources of strain, viz., contraction due to the collapse of the gel crystal lattice as a direct result of the loss of chemically combined water, and contraction due to the sintering of solid gel particles aided by the elevated temperature and time at temperature. An estimate of the contribution of sintering to the total
observed contractive deformation can be obtained by assuming that the $\epsilon_{w_n}$ versus $w_n$ curve of the rapidly heated pastes (Heating Schedule C and C') up to the point where the 500 F temperature was reached represents only deformation due directly to loss of $w_n$—there being little time for contraction due to sintering to make any substantial contribution. Extrapolation of these data points to $w_n = 100$ leads to the conclusion that over half of the total contraction deformation exhibited by the pastes during their loss of $w_n$ might actually be contraction due to the proposed sintering phenomenon.

Significantly, the end point contraction is nominally the same for all the pastes studied which supports the contention that $\epsilon_{w_n}$ is a constant for the cement used in the study.

**Sintering in Heated Cement Paste**

Cement gel may be considered as a metastable system of finely divided particles; the system as a whole being one of extremely high, free surface energy. The system approaches a more stable lower energy form by a reduction in surface area which comes about through the coalescence or merging of the small particles into larger ones and the contraction of intersolid gaps. In pastes subjected to drying at normal ambient temperatures expulsion of portions of the evaporable water causes solid gel surfaces to merge resulting in overall inelastic contraction. Inasmuch as the system has gone from a higher to a lower energy level, this process is irreversible. This irreversible contraction (the irreversible component of shrinkage) is a manifestation
of the fact that a metastable system is progressing toward a stable lower energy level. Most workers in the field do not usually refer to the phenomenon just discussed as sintering but rather refer to a coalescence or merging of particle surfaces in hydrated cement systems at normal ambient. In any event considerable experimental evidence is available which demonstrates this behavior in cement pastes.

Chandra, et. al., determined in a study of the mechanical properties of compacts of hydrated cement that: during mechanical compaction chemical bonds are formed when solid elements of the hydrated paste gain mutual contact. The strength of the paste can be described as being derived from the proximity of much of the very large surface.

In view of the past discussion it is apparent that solid-solid bonding between gel particles does occur in cement pastes at normal temperatures either through the effects of drying or the applications of external stress. No one has appeared to question the effect of elevated temperature on this process. However, it can be demonstrated that the driving force for the reduction of surface area in hardened cement paste should be increased at elevated temperatures. The results of the present study on compacts of heated, hydrated cement pastes are offered as direct proof that solid-solid bonding occurs in cement pastes as a sole consequence of the effect of elevated temperatures. The studies of surface area change in heated pastes support this contention. The effect of heating compacts of hydrated cement for
20 hours or 9 days at 500 F was to increase (a statistically significant increase) the compressive strength of the paste by about 25 percent. Inasmuch as the material making up the compacts had been previously heated to equilibrium at 500 F, no chemical changes occurred in the compacted material on reheating to 500 F. The only physical factor that could possibly account for the increase in strength is an increase in the degree of bonding of the cementitious phase. The development of these bonds was further evidenced by a linear shrinkage of the specimens during heating; again, it is pointed out, in the absence of any concomitant chemical change in the paste. Additional evidence is provided by the fact that the simultaneous application of heat (500 F) and pressure resulted in still further increases in strength of the compacts. The final experimental finding in support of the sintering hypothesis is the fact that the heating of cement pastes brought about a 40 to 50 percent reduction in their specific surface area relative to measurements made after vacuum drying at normal temperatures. Measurements on pastes heated to 175 F demonstrate that this reduction was due solely to the effect of elevated temperature inasmuch as no chemical change occurred in this sample at 175 F. Only the elimination of surfaces previously accessible to the N₂ molecule can account for this observation.

It is suggested that the solid-to-solid bonding demonstrated for the hydrated paste compacts also occurred during heating to 500 F in the hardened pastes used in the present study. This creation of solid-solid bonds resulted in contractive deformations occurring in the
heated paste specimens which must be distinguished from the contractive deformations resulting from the loss of \( w_e \) and \( w_n \) from the pastes during heating. Inasmuch as elevated temperatures were involved in the formation of these bonds, it is thought that reference to the observed behavior as a sintering phenomenon is not inappropriate. The postulated solid-solid bonding of gel surfaces in unstressed cement paste as elevated temperatures is envisioned as being completely akin to the solid-solid bonding that occurs during drying shrinkage of cement paste at normal temperatures. Elevated temperature then assumes the role of an additional driving force for a process that is operative at normal temperatures; much in the same manner that an external compressive stress aids the process at normal temperatures (increased creep during drying). A portion of the additional solid-solid bonds formed as a result of the sintering process should be strong enough to resist disruption when a heated paste is resaturated with water so that the irreversible contraction of a heated paste should exceed the irreversible shrinkage of a comparable paste dried at room temperature.

**The Effect of Aggregate on the Deformation of Cement Paste During Heating**

Studies of the mortar demonstrated that the presence of 50 volume percent of an inelastic, solid dispersed phase in the 0.45 paste greatly diminished the contractive deformations of the paste throughout its heating history. A similar effect has been observed regarding the effect of aggregate on the drying shrinkage of concrete.
Hobbs\(^{53}\) has derived a formula from fundamental considerations for expressing the shrinkage of concrete as a function of the aggregate content, as follows,

\[
S = S_0 \left[ \frac{k_M + k_A - 2gk_A}{k_M + k_A} \right] + S_A \left[ \frac{2gk_A}{k_M + k_A} \right]
\]  \hspace{1cm} (6)

where

- \(S\) is the shrinkage of the concrete
- \(g\) is the volume of aggregate per unit volume of concrete
- \(S_0\) is the shrinkage that would occur if no aggregate were present
- \(S_A\) is the shrinkage of the aggregate
- \(k_M\) is the bulk modulus of the matrix (paste)
- \(k_A\) is the bulk modulus of the aggregate

Using Equation (6) the shrinkage ratio for concrete \((S/S_0)\) is shown plotted in Figure 35 versus aggregate volume concentration. It was assumed that \(\mu = 0.2\), \(k_A = 4k_M\), and \(S_A \ll S_0\). The actual data points are those of Pickett.\(^{51}\)

For an aggregate volume \(g = 0.5\) (as for the mortar), the predicted value of shrinkage from Equation (6) is

\[
S/S_0 = 0.20
\]

The actual value of the mortar shrinkage ratio was,

\[
\frac{S}{S_0} = \frac{0.13}{0.7} = 0.19
\]

which is in quite close agreement.
Figure 35. Variation of the shrinkage ratio for concrete with aggregate volume concentration.
It was of interest to determine whether Equation (6) could be used to predict the ratio of the permanent contraction of the mortar specimens \( \varepsilon_{\text{tot}}(\text{mortar}) \) relative to the permanent contraction of the 0.45 paste specimens \( \varepsilon_{\text{tot}}(0.45 \text{ pastes}) \) for the various heating schedules employed, i.e., \( \frac{\varepsilon_{\text{tot}}(\text{mortar})}{\varepsilon_{\text{tot}}(0.45 \text{ paste})} \). Data summarizing these calculations are shown in Table 15. It is claimed that these results are in reasonable agreement with the predictions of Equation (6). The fact that all the measured values are somewhat less than the predicted value may be due to the fact that in the heated specimens the factor \( g \) changes during the test inasmuch as the aggregate volume is increasing while the composite volume (the specimen itself) is decreasing. Reference to Equation (6) shows that with an increase in aggregate volume \( (g) \), the factor \( S/S_0 \) should decrease.

**TABLE 15**

COMPARISON OF PREDICTED AND MEASURED CONTRACTION OF HEATED MORTAR

<table>
<thead>
<tr>
<th>Mortar Specimen Identification and Heating Schedule</th>
<th>Predicted ( S/S_0 ) from Equation (6), percent</th>
<th>Measured Values of ( \varepsilon_{\text{tot}}(\text{mortar}) )/( \varepsilon_{\text{tot}}(0.45 \text{ paste}) ), percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC-4_1 C</td>
<td>0.20</td>
<td>.18/1.1 = .16</td>
</tr>
<tr>
<td>MC-4_2 A</td>
<td>0.20</td>
<td>.20/1.52 = .13</td>
</tr>
<tr>
<td>MC-4_3 C_v</td>
<td>0.20</td>
<td>.28/1.78 = .16</td>
</tr>
</tbody>
</table>
The primary implication of these findings is that the effect of aggregate on the contraction of concrete during heating is similar to the effect of aggregate on the shrinkage of concrete during normal drying, i.e., the aggregate acts primarily as a restraint to contraction. However, the overall consideration is somewhat more complex in that during heating the aggregate volume increases while that of the paste decreases. On this basis the variation in permanent contraction of the mortar with heating rate should be controlled by the temperature-water loss relationship during the period of evaporable water loss in much the same manner as was observed for the 0.45 cement pastes. The deformation behavior of the mortars during subsequent heating (after \( w_e \) gone) should be substantially similar and independent of heating rate. That this was the case is claimed by the data in Figure 34.

It should be possible to predict the permanent contraction of the mortars using the same relationship derived for the paste specimens, viz.,

\[
\varepsilon_{\text{tot}} = \left[\frac{\Delta L}{L_0}\right]_{w_e} + \varepsilon_{\text{wn}}^{*} + \alpha\Delta T
\]

using the appropriate value of \( \varepsilon_{\text{wn}}^{*} \) and \( \alpha \) for the mortar. This is done in Table 16.
TABLE 16
MEASURED AND CALCULATED VALUES OF THE PERMANENT
CONTRACTION OF HEATED MORTAR SPECIMENS

\[ \varepsilon_{\text{tot}} = \left[ \frac{\Delta L}{L_0} \right]_{w_e}^* + \varepsilon_{w_n}^* + \alpha \Delta T \]

<table>
<thead>
<tr>
<th>Mortar Specimen Identification and Heating Rate</th>
<th>[\frac{\Delta L}{L_0}]_{w_e} percent</th>
<th>\varepsilon_{w_n}^* percent</th>
<th>\alpha \Delta T, percent</th>
<th>Permanent Contraction, \varepsilon_{\text{tot}} percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC-41 (C)</td>
<td>- .111</td>
<td>.101</td>
<td>.20</td>
<td>.190</td>
</tr>
<tr>
<td>MC-42 (A)</td>
<td>.016</td>
<td>.086</td>
<td>.105</td>
<td>.207</td>
</tr>
<tr>
<td>MC-43 (C')</td>
<td>- .005</td>
<td>.118</td>
<td>.15</td>
<td>.263</td>
</tr>
</tbody>
</table>

Dimensional Instability of Heated Concrete. As regards concrete, there is experimental evidence which suggests that the intrinsic strength of the aggregate in concrete may be an important factor in influencing the deformation of the concrete during initial heating. In lightweight concretes where weak, porous aggregates are employed, the strength of the aggregate may be exceeded before the yield strength of the paste is reached during heating as the aggregate expands and the paste contracts. In that case, the contracting paste actually crushes the aggregate and the overall deformation of the concrete during heating is a contraction. This phenomenon has been shown for vermiculite concretes (see Figure 9) which also shows that
as the cement factor is increased, the contraction is increased) and for concretes containing expanded slag as the aggregate.

The effect of an external stress on the deformational behavior of heated concrete is amenable to explanation in terms of a highly mobile matrix phase as evaporable water is being removed. In stressed (compressive stress) concrete that is heated for the first time the aggregate undergoes expansion as in the case of unstressed heated concrete. However, the effect of the external compressive stress is to compact the gel phase which yields to the stress and the overall concrete deformation is a contraction. It is expected that the magnitude of deformation (contraction) of stressed concrete on initial heating will be in proportion to the magnitude of the imposed stress.

Drawing upon the results of the present study and the results of previous investigations it is possible to predict qualitatively the deformational behavior of concrete that can be expected under a wide variety of environmental conditions where the ultimate concrete temperature is 500 F. This is depicted graphically in Figure 36 which shows the extremes of deformation that could possibly occur under any conditions of heating and loading. Unstressed and unrestrained concrete, heated from room temperature in the saturated state to 500 F will exhibit an expansion. The actual magnitude and rate of this expansion will depend upon:

1. The heating rate.
2. The specimen size.
3. The thermal expansion of the aggregate.
4. The strength of the aggregate.
5. The volume percent aggregate in the concrete.
Unstressed concrete heated rapidly from room temperature to 500 F from the saturated state—no imposed stress or restraint.

Concrete heated very slowly from room temperature to 500 F from the saturated state with an imposed compressive stress of large magnitude.

Figure 36. Hypothetical description of the inelastic deformational behavior of heated concrete.
The greatest possible expansion will occur when the heating rate is at a maximum, the specimen size is large, and the concrete is made up of a high strength, high expansion aggregate that comprises the maximum volume percent of the concrete consistent with adequate workability. Dimensional stability will be achieved in this concrete following the removal of all the evaporable water and that portion of the nonevaporable water not stable at temperatures below 500 F, and after sintering has ceased to be operative. If maintained at 500 F, this concrete will exhibit a permanent expansion.

The other extreme of deformational behavior of heated concrete is represented by saturated concrete that is heated from room temperature to 500 F with an imposed compressive stress of high magnitude. Under these conditions the concrete will exhibit an initial and continuing contraction with time. The magnitude and rate of this contractive deformation will depend upon the five factors discussed previously for unstressed concrete and, in addition, upon the magnitude of the compressive stress and the time in the concrete’s heating history when the stress is applied.

The greatest possible contraction will occur when the concrete is loaded in the saturated state at room temperature, when the heating rate is at a minimum, the specimen size is large; and the concrete contains a low strength aggregate having a low coefficient of thermal expansion and has a relatively high cement factor.
For all other conditions of heating and loading imaginable, the plot of concrete deformation versus time should fall between the extremes represented by the curves in Figure 36 with several exceptions:

1. If a saturated concrete, under a tensile stress at room temperature, is subsequently heated to 500 F, the rate and magnitude of expansion exhibited by the concrete during heating could exceed that depicted by the curve for unstressed concrete in Figure 36. This situation was not considered in view of the fact that concrete structures are designed to minimize the chance of occurrence of large tensile stresses.

2. If the specimen size is large enough, it is conceivable that the temperature of the concrete could rise above 212 F prior to the complete expulsion of evaporable water from the concrete. Under these conditions the mineralogy of the hydrated cement phase can undergo a drastic change. Very broadly this change can be categorized as a change from an amorphous to a more crystalline state. It is expected that this event would result in decreased mobility of the gel phase during the expulsion of evaporable water.

If the temperature of the concrete is increasing at the same time that the paste is contracting due to loss of nonevaporable water, it is expected that this will have deleterious effects on the cohesion of the paste phase inasmuch as the paste cannot accommodate the increasing aggregate volume through ductile yielding as it could when evaporable water was being lost.

Concrete (both loaded and unloaded) maintained at temperatures up to 500 F for periods of time sufficient to produce dimensional stability should behave elastically on subsequent cycling of temperature or stress provided that the stress originally on the concrete is not exceeded and the highest temperature of exposure of the concrete is not exceeded.
However, inasmuch as the coefficient of thermal expansion of the matrix phase and the aggregate phase may not be the same in concrete maintained for long times at temperatures up to 500 F, the cooling of the heated concrete though elastic on a macro scale can result in stresses in the matrix phase at room temperature. If \( \alpha_{\text{aggregate}} \) is greater than \( \alpha_{\text{matrix}} \), the matrix will contract normally. If \( \alpha_{\text{aggregate}} \) is less than \( \alpha_{\text{matrix}} \), the matrix will be in a state of tension at room temperature (assuming a heat stable aggregate is used). It is suggested that the deterioration in strength of concrete through thermal cycling would be expected to be greater in concretes containing aggregates having coefficient thermal expansion considerably less than that of cement paste free of evaporable water (which is \( \approx 6.0 \times 10^{-6} \text{ in/in/F} \)). This has been demonstrated in studies on concretes containing limestone aggregate (\( \alpha \approx 3.0 \times 10^{-6} \)), dolerite aggregate (\( \alpha \approx 3.8 \times 10^{-6} \)), and firebrick aggregate (\( \alpha \approx 6.0 \) to \( 7.0 \times 10^{-6} \)).
III. SUMMARY AND CONCLUSIONS

The effects of exposure to temperatures up to 500 F on the dimensional stability of portland cement paste and mortar was investigated. The impetus for this work was provided by a general lack of understanding of the effect of heat exposure on the behavior of portland cement concrete, particularly as related to its use in a prestressed-concrete-pressure-vessel (PCPV) reactor.

Changes in linear dimension and weight were measured simultaneously in small, cylindrical specimens of cement paste and mortar heated to 500 F at atmospheric pressure using various heating schedules. The study was undertaken in such a manner as to define more precisely the role of free and chemically combined water in the paste relative to the deformational behavior of cement paste during heating.

The results of the present study and of previous studies by the author and others permit the following conclusions to be drawn regarding the effect of heat exposure on the dimensional stability of portland cement concrete.

1. Portland cement concrete heated at atmospheric pressure to temperatures up to 500 F exhibits considerable volume instability. The environmental and body parameters that directly or indirectly influence the nature and magnitude of this instability include:
2. The volume instability exhibited by concrete during heating is a direct consequence of the dimensional changes occurring in the cement paste phase due to concomitant chemical changes and the physical effects of elevated temperature exposure.

3. Numerous sources of deformation may be operative in concrete heated for the first time, including:

(a) Thermal expansion strain of the cement paste and aggregate phase
(b) Contraction accompanying the loss of evaporable water from the cement paste
(c) Contraction accompanying the loss of nonevaporable water from the cement paste
(d) Contraction accompanying a densification of the cement paste brought about by a phenomenon akin to solid state sintering
(e) Contraction accompanying a densification of the cement paste brought about by the presence of compressive stresses during the removal of evaporable water from the concrete
(f) Expansion accompanying a decrease in cement paste density brought about by the presence of tensile stresses during the removal of evaporable water from the concrete
(g) Contraction due to the presence of an external compressive stress in dry concrete (void of evaporable water), i.e., high temperature creep
4. The cement paste phase in concretes heated for the first time exhibits considerable mobility during the time in which evaporable water is being expelled from the paste. This is the factor that is primarily responsible for the considerable differences in deformational behavior exhibited by concretes of similar composition when heated to 500 F under varied conditions of heating and loading. Depending on the internal and external forces that are operating on the cement paste phase during this time, the concrete may either expand or contract.

5. Unstressed cement pastes and concrete exhibit a permanent dimensional change on heating at temperatures up to 500 F which can be predicted through the use of the empirically derived relationship,

\[ \varepsilon_{\text{tot}} = \left[ \frac{\Delta L}{L_0} \right]_{\text{e}}^* + \varepsilon_{\text{w}}^* + \alpha \Delta T \]  

Equation (4) is applicable to any cement paste or concrete that has been exposed to the same maximum temperature (500 F in this case) for approximately the same length of time. The usefulness of equation (4) in predicting the permanent dimensional change in heated cement pastes and concretes probably applies to other temperatures of exposure in addition to 500 F.
It appears likely that once $\varepsilon_{\text{tot}}$ has been determined for an unstressed cement paste subjected to a given heating schedule, it will be possible to predict $\varepsilon_{\text{tot}}$ for concretes made using the same paste, through utilization of existing equations relating concrete shrinkage to concrete aggregate content.

6. The total contractive deformation in heated paste or concrete accompanying the removal of nonevaporable water from the paste $\left[\varepsilon^*_w\right]$ is a constant for any given paste or concrete specimen that is exposed to the same final maximum temperature, regardless of the prior thermal history of the specimen.

7. Significant microstructural changes take place in heated cement pastes which are influenced by the temperature level of exposure and by forces acting on the paste while it is exposed to elevated temperatures. This finding prompts a word of caution regarding the indiscriminate use of elevated temperatures as a means of varying the evaporable water content of pastes in studies on cement pastes or concretes.
APPENDIX A

Fabrication of Cement Paste and Mortar Specimens

All specimens for the study were prepared by casting cement-water or cement-water-quartz mixtures into glass test tubes. The low water content cement paste (w/c, 0.33) and the mortar were mixed using a planetary mixer. The mixing time and sequence of adding materials was the same for all the batches prepared. The higher water content pastes were mixed using a Waring Blender. Again, the mixing time and sequence of adding materials were the same for all the batches prepared.

Precautions were taken to minimize moisture loss from the pastes during specimen fabrication. The batch size employed for the pastes was 700 or 1,000 grams (cement weight) and for the mortar was 870 grams (dry mix weight).

Cylindrical specimens were formed by casting the wet mixes into glass test tubes (5/8-inches in inside diameter by 7 inches long). Consolidation of the material in the molds was facilitated by the use of a small vibrating table. Entrained air in the specimens was eliminated or minimized by one of two techniques, viz.,

1. A slight vacuum was pulled on the tubes contained the dense paste (w/c, 0.33) or the mortar during the vibrating step. Material was added to the molds in four roughly equivalent portions. Following the introduction of each portion of fresh material to the mold, a moderate vacuum was applied and held for about 20-30 seconds. A mechanical vacuum pump was used for this purpose. Vacuum was applied to the test tube with the aid of a two-hole
rubber stopper through which passed the line leading to the roughing pump. The other hole in the stopper permitted the vacuum in the tube to be broken at will. The procedure employed in the preparation of each specimen was nominally the same in terms of vibrating time and frequency, material addition, and vacuum time and sequence. It was determined that actual losses of water from the tubes due to the application of vacuum were negligible. The procedure resulted in the preparation of virtually air-free specimens.

Air-free specimens of pastes with higher water contents (w/c of 0.45 or 0.60) could not be prepared using the vacuum technique due to vigorous agitation of these relatively wet mixtures caused by the vacuum. Specimens with low entrained air contents were prepared by pouring the wet mixes into the molds (which were being vibrated) in a very fine stream. This procedure, although time-consuming, permitted most of the entrained air bubbles to migrate close enough to an exposed surface to break.

Normally, six cylindrical specimens were prepared from each batch. A total of 23 batches were prepared for the study, including 10 of 0.33 w/c paste, 4 of 0.45 w/c paste, 5 of 0.60 w/c paste; and 4 of the mortar. The specimens, after casting, were placed and maintained in a moist closet which provided an environment of 71 to 76 F and 100 percent relative humidity.

The removal of the hardened cylinders from the glass test tubes presented somewhat of a problem. The dense paste specimens (w/c, 0.33) were removed by carefully cracking the glass tubes in a vice. This procedure could not be used to remove the other specimens, however, as they invariably broke. This difficulty was finally overcome by casting the less dense pastes and the mortar in precracked glass-test tubes which were prepared as follows: the tube was
wrapped firmly with cellophane tape and then was placed in a vice and carefully cracked. The cracked tube was then coated inside and out with paraffin to provide air and water-tightness. Specimens were easily removed from these molds. All specimens were cured in the test tubes in the moist closet for 60-80 days prior to use in the study.
APPENDIX B

Procedures Used in Analytical Studies of Cement Pastes

a. Each cylindrical cement paste specimen as-cast was cut into five roughly equal lengths which were labeled 0, 1, 2, 3, and 4, with 0 being the top of the cylinder (relative to the casting position) and 4 the bottom.

b. The length labeled '0' was discarded.

c. Pieces of 1, 2, 3, and 4 were obtained and were used individually in the determination of density.

d. Determinations of evaporable water, nonevaporable water and specific surface area were made on composite samples of 1, 2, 3, and 4 that had been crushed to minus 30, plus 80 mesh and blended.

The effect of heat exposure on evaporable and nonevaporable water content and specific surface area of the paste was studied using both crushed samples (-30, +80 mesh) and full-sized cylinders.

Measurements of Evaporable and Nonevaporable Water

The evaporable and nonevaporable water content of the pastes was determined for saturated specimens prior to heating and for specimens heated for 48 hours at 250°F and 500°F. These measurements were obtained using the vacuum drying technique of Copeland and Hayes. Samples were prepared for analysis by crushing to minus 30 mesh, plus 80 mesh in a CO₂-free atmosphere. The crushed samples (both as-cured and heated) were subjected to vacuum drying over ice at dry ice temperature (-79°C) for four to five days' time. The water removed during
this time is by convention the evaporable water content of the paste.

The nonevaporable water content of the pastes was determined by igniting the sample previously vacuum dried to 1050 C. The weight loss on ignition was due to loss of chemically combined water plus the normal L.O.I. of the anhydrous cement. A correction was made for the latter. The nonevaporable water content of the pastes was obtained using the relationship:

\[ \frac{w_n}{c} = \frac{w_1}{w_2} (1-I) - 1 \]

where

- \( w_1 \) is the paste weight before ignition to 1050 C
- \( w_2 \) is the paste weight after ignition
- \( I \) is the L.O.I. of the raw cement in gms per gm of cement

**Surface Area Measurements**

Measurements were made of the specific surface area of the cement pastes in the as-cured state and after heating for 48 hours at 175, 250, 375, and 500 F. Surface area measurements were obtained using a Stohlein area-meter which utilizes a modified B.E.T. procedure (low temperature nitrogen gas adsorption). The samples used in this determination were 1.0 to 2.0 gram samples of minus 30, plus 80 mesh paste. The procedure used in measuring specific surface area was as follows:

a. As-cured pastes (after vacuum drying) and heated pastes were first degassed for 24 hours at 75 F by subjecting them to a sustained flow of dry nitrogen

b. Two glass vessels of nominally equal volume, one empty and one containing the paste samples are brought to temperature equilibrium at normal ambient temperature. Both vessels contain 100 percent dry nitrogen at ambient atmospheric pressure
c. Both vessels are immersed in liquid nitrogen and allowed to equilibrate. Then a differential manometer linked to both vessels is opened. The gas pressure in the sample vessel is decreased relative to the empty vessel due to the adsorption of gas by the sample. The pressure differential is used to calculate the surface area as is shown in the following calculation example

d. Sample calculation:
Atmospheric pressure \( (P_b) \) at time of test = 744.22 mm
Measured pressure differential \( (\Delta P) \) = 101 m;
Sample weight \((m)\) = 2.0057 gms

First, the equilibrium pressure \( (P) \) is calculated using the relationship:

\[
P = C_1 P_b - C_2 \Delta P
\]

where \( C_1 = 0.2782 \) and \( C_2 = 0.077 \) are machine constants.

\[
P = 0.2782 (744.22) - 0.077 (101)
\]

\[
P = 199.265
\]

The surface area \( (\phi) \) is then calculated using the relationship:

\[
\phi = 0.0021 \left\{ \frac{(785-P)}{m} \cdot \Delta P \right\} \left[ k_1 + k_2 P \right]
\]

where \( k_1 = 0.1027 \) and \( k_2 = 6.65 \times 10^{-5} \)

\[
\phi = 0.0021 \left[ \frac{785-199.265}{2.0057} \cdot 101 \right] \left[ 0.1027 + 6.65 \times 10^{-5} \cdot 199.265 \right]
\]

\[
\phi = 7.2 \, \text{m}^2/\text{gm}
\]

**Porosity Determinations**

The initial water/cement ratios of the pastes used in this study were chosen so as to yield specimens having a range of paste...
porosities. Calculations of paste porosities were made using data obtained in the analyses of evaporable and nonevaporable water. The relationships used in these calculations were primarily those derived by Copeland and Hayes.54

The equations expressing porosity in terms of volume percent of the cement paste which were used were as follows:

For total porosity ($V_p^t$)

$$V_p^t = \frac{V_t}{V} = 0.99 \left[ \frac{w_t - w_n}{c} \right] \left[ \frac{d_p}{w_t} \right] \left[ \frac{1}{1 + \frac{w_t}{c}} \right]$$ (10)

For capillary porosity ($V_p^c$)

$$V_p^c = \frac{P_c}{V} = 0.99 \left[ \frac{w_t}{c} - (1 + 2.38k) \frac{w_n}{c} \right] \left[ \frac{d_p}{w_t} \right] \left[ \frac{1}{1 + \frac{w_t}{c}} \right]$$ (11)

where $k$ is an empirical constant which for Type I cements cured at $\approx 70^\circ F$ may be considered to be 0.3318.

Inasmuch as the pastes were prepared air-free, the gel porosity ($V_p^g$) was determined by difference $[(P_t - P_c)/V]$. 

**Determination of Paste Composition**

The volume of unreacted cement in the paste specimens at the time of testing was calculated from the relationship:5

$$V_{uc} = \frac{1 - \frac{w_n}{c}}{0.26} V_c$$ (12)

The factor 0.26 is the grams of nonevaporable water per gram of cement in a fully hydrated Type I cement paste.

The volume percent of the solid hydrated cement phase $V_{hc}$ in
a sample of cement paste was then determined from the relationship:

\[ V_{hc} + V_{uc} + V_{p} = 1.0 \]  

(13)

**Measurement of Paste Density**

The density of the pastes \( d_p \) was determined on saturated samples using the water displacement technique. First, the bulk volume \( V \) of the paste was determined as follows:

\[
V = \frac{\text{Saturated Weight of Sample (gms)} - \text{Weight of Sample (gms)}}{\text{Specific Gravity of Water at test Temperature}}
\]  

(14)

Paste density was then calculated as:

\[
d_p = \frac{\text{Saturated Weight of Sample (gms)}}{V \text{ (cc)}}
\]  

(15)
REFERENCES


