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<https://doi.org/10.18297/etd/1838>

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University of Louisville

Physical Properties of Silica-Plaster Mixtures

A Thesis

Submitted to the Faculty

of the Graduate School

in Partial Fulfillment of the

Requirements for the Degree of

Master of Science in Chemical Engineering

Department of Chemical Engineering

By

Robert Neiman

1935

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Thermal Expansion of Silica-Plaster Mixtures

	% Silica	% Plaster	
11.		100.00	80
12.	20.00	80.00	81
13.	40.00	60.00	82
14.	60.00	40.00	83
15.	70.00	30.00	84
16.	80.00	20.00	85
17.	90.00	10.00	86
18.	97.00	3.00	87
19.	Thermal Expansion of Plaster-Silica Mixtures (1300°F.)		

List of Curves (Cont.)

Curve No.

Page

Thermal Expansion of Mixtures of Silica,
Plaster and other Materials.

	% Silica	% Plaster	% Material		
20.	60.00	30.00	10.00	Titanium Dioxide	89
21.	60.00	30.00	10.00	Sodium Silicate	90
	50.00	30.00	20.00	Sodium Silicate	
22.	60.00	30.00	10.00	Calcium Fluoride	91
23.	60.00	30.00	10.00	Zinc Oxide	92
24.	68.00	30.00	2.00	Boric Acid	93
25.	60.00	30.00	10.00	Chromic Oxide	94
26.		3.00	97.00	Chromic Oxide	95
27.	60.00	30.00	10.00	Cristobalite	96
28.	67.00	30.00	3.00	Lithium Carbonate	97
	69.00	30.00	1.00	Lithium Carbonate	
	65.00	30.00	5.00	Lithium Carbonate	
29.	60.00	30.00	10.00	Beryl	
30.	60.00	30.00	10.00	Calcium Silicate	99
31.	69.60	30.00	.35	Vermiculite	100
	68.40	30.00	1.50	Vermiculite	
	60.00	30.00	10.00	Vermiculite	
32.	60.00	30.00	10.00	Aluminum Oxide	101
33.	60.00	30.00	10.00	Chromite	102
34.	60.00	30.00	10.00	Barium Sulfate	103
35.	60.00	30.00	10.00	Feldspar	104
36.	60.00	30.00	10.00	Metronite	105

List of Curves (Cont.)

Curve No.

Page

	% Silica	% Plaster	% Material	
37.		3.00	97.00 Anhydrite	106
38.		100.00	Plaster	107
		3.00	97.00 Anhydrite	
		3.00	97.00 Gypsum	
39.	60.00	30.00	10.00 Wellastonite	108
40.	60.00	30.00	10.00 Magnesium Oxide	109
41.	69.90	30.00	.10 Lithium Fluoride	110
	69.80	30.00	.20 Lithium Fluoride	
	69.00	30.00	1.00 Lithium Fluoride	
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ACKNOWLEDGMENT

**The Author Wishes to Express
His Appreciation for
The Kind and Helpful Suggestions
Given by Dr. R. C. Ernst
Who Directed This Research**

ACKNOWLEDGMENT

The Whip - Mix Industrial Research Fellowship

The author wishes to express his appreciation to the Whip-Mix Corporation, 411 W. Avery Street, Louisville, Kentucky, for the fellowship granted and for the apparatus and chemicals furnished.

The author wishes to express his many thanks to Mr. E. A. Steinbock, President of the Whip-Mix Corporation for the many suggestions offered and for time spent in familiarizing the author with the commercial aspects of the materials.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the suggestions and samples so kindly given by the following individuals and concerns:

Bureau of Standards

The Carborundum Co.

M. C. Dailey, United States Gypsum Co.

Foots Mineral Co.

Dr. J. Jungmann, American Fluoride Corp.

The Norton Co.

Pacific Coast Borax Co.

Dr. E. Sohn, Standard Sanitary Co.

CHAPTER I

INTRODUCTION

INTRODUCTION

Silica (SiO_2) and Plaster ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) are two of the oldest nonmetallic minerals known to mankind. The former ranks next to the feldspar group as the most abundant mineral in the earth's crust. It is found in all parts of the globe and is known to every one in the form of sand. Because of its properties of being hard, tough, refractory, resistant to acids, and often transparent it is admirably suited for use as an abrasive, refractory material, manufacture of glass and chemical ware, and as an inert filler, or aggregate.

Plaster, frequently called Plaster of Paris, so named because it was obtained by burning gypsum from deposits in the Paris basin, is made by calcining gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) until $1\frac{1}{2}$ molecules of water are driven off. The chief value of the resulting material in the arts and industries lies in the fact that when mixed with water it forms a plastic mass which can be moulded, cast, pressed, or otherwise made into any required shape or form. Within a short time the $1\frac{1}{2}$ H_2O of hydration are again absorbed and the mass reverts (sets) to the original crystalline gypsum condition, a hard and strong material. Due to this property plaster finds wide use in a number of industries. A few of its specific uses include wall plaster, pottery plaster as moulds for ceramic materials and casting moulds.

By combining the two materials whereby the silica is the filler and plaster the binder, materials with a wide variety and range of properties are produced which are suited for uses where either alone would fail.

It was the purpose of this investigation to study the Thermal Expansion, Setting Expansion, Setting Time, and Tensile Strength of silica and plaster mixtures with varying amounts of water. The effect of the substitution of other materials for all or part of the silica on the above properties was also studied. An interpretation of the results from a chemical and physical standpoint is given.

CHAPTER II

HISTORICAL

HISTORICAL

Silica

Silica in the form of sand has been known to civilisation since the beginning of time. Rock crystal was probably the sixth precious stone, (adamos) (diamond) described in Exodus as adorning the breastplate of the High Priest of Israel.

The early Greek philosophers were of the opinion that minerals and earths were formed from water. Theophrastus thus opens his essay "On Stones" - (Everything formed in the earth has its origin either from earth or from water. Water is the base of all metals."

Pliny (A.D.77), in his "Historical Naturalis", translates the Grecian term for ice used by Theophrastus as "crystallus". This term was specifically applied to quartz or rock crystal because - "Crystal assumes a concrete form from excessive congelation."

G. Agricola said that rock crystal was not ice but a denser product of cold.

R. Boyle (1) disagreed with the above. He argues thus - "I found silica to have a density of two and two-thirds that of water, and furthermore the torrid zone abounds in crystal."

The ancients were familiar with the art of producing glass by fusing rock crystal or sand with salts of Sodium and Potassium.

Silica's resistance to fusion and chemicals retarded the developments of its chemistry immensely. Scheele's discovery of hydrofluoric acid in 1771 proved a veritable

touchstone to the chemistry of Silica, but even then it was slow.

In 1666, O. Tachenus pointed out that, unlike earths, silica has acidic properties, since it combines with alkalies but shows no tendency toward neutralizing acids.

C. W. Scheele, in 1771, regarded silica earth as a compound of hydrofluoric acid and water because the gas obtained when fluorspar is heated in a glass retort with sulfuric acid gives a precipitate of silica when passed into water. This was later disproved when the same materials were heated in a lead or non-silicious retort.

T. Bergmann (2) separated silica from siliceous earths by fusing them with alkali carbonate or hydroxide, and treating the product with dilute acid, whereby insoluble silica and soluble alkali salts are formed.

Lavoisier, (3) in 1787, assumed silica to be an oxide of an unknown metal.

In 1808, J. J. Berzelius, in a letter to H. Davy, stated that in making an analysis of cast iron, he found a metal that took up half its weight of oxygen. He decomposed silica by heating with iron and charcoal, forming an alloy of iron and silica now known as ferrosilicon.

In 1809, H. Davy (4) attempted to isolate the metal by the electrolysis of silica, or by reduction with potassium at a red heat. He said that had he been so fortunate as to have isolated the metal he would have proposed for it the name "silicium".

J. J. Berzelius, in 1811, showed that silica unites with bases in definite proportions, forming salts of silicic acid, and that siliceous minerals are to be regarded as definite salts of this acid.

J. J. Berzelius finally succeeded in producing the element by reducing potassium fluosilicate, K_2SiF_6 , with potassium, he also determined its atomic weight and proposed the name Kiesel, but it was not adopted.

During the 19th century, science made great strides in developing experimental methods for studying the properties of matter. Nearly everyone who invented a new apparatus or method found silica in the form of quartz a convenient standard substance on which to try his experiment or invention. There are always a few specimens of quartz about a research laboratory and there is not a museum which does not have a specimen or two of rock crystal. Next in furnishing an abundance of available data comes vitreous silica which is of untold value scientifically and commercially.

Probably the most widely studied property of quartz is its crystalline form and internal structure. One of the most complete monographic studies that has

ever ever been made on a mineral species was that of Des Cloiseaux (5) in 1855. Just preceeding this study, Rose (6) published an important study on this subject, illustrated with 51 engraved figures.

In 1864, H. Fizeau (7) devised the interferometric method of measuring the dilatation of materials. By this method a specimen 1 to 10 mm. long is used and the change in length is measured in terms of the wave length of monochromatic light, by counting the number of interference fringes produced between two reflecting surfaces. This method became popular with a host of experimentors since the small size of specimen needed makes a number of materials which form small sized crystals available for study.

Probably the most accurate absolute measurements ever made of any substance are those of Macé de Lépinay, Buisson, and Benoit (8) on Quartz. These were made from 1905 to 1910 at the International Bureau of Weights and Measures. The results on two specimens gave 2.650667 and 2.650571 as the density of quartz at 0°C.

In 1861 Vem Rath (9) announced the discovery of a new crystalline form of silica, which he named "tridymite". It was found in a rock from Cerro San Cristobol, Mexico. It occurred in colorless crystals 1 mm. or less in diameter. Once identified and described this new mineral was found in a considerable number of places, chiefly in eruptive rocks in France and Germany.

In 1887 Vom Rath (10) announced the discovery of a new mineral. It had been found by others as early as 1800 but was thought to be spinel.

In 1889 Le Chatelier (11) discovered the high-low inversion of quartz.

In 1890 Mallard (12) gave cristobalite a standing among well-recognized minerals. His measurements of optical properties and especially his discovery of a high-low inversion proved that it was a form distinct from tridymite.

Thus, by 1890 the principal modifications of silica were fairly well established. The most important recent advances were by Fenner (13) who cleared up the disputed questions regarding the stability relation and high-low inversion.

With the discovery of the value of X-Rays in studying crystal structure, W. H. Bragg (14) made a valuable present to modern science. His studies on the structure of silica are very noteworthy. Others who studied the structure of the various forms of Silica include Kyropoulos 1917 (15), Gibbs, (16), Maugin (17), and Wyckoff (18), in his Monograph on the Structure of Crystals, 1924.

PLASTER

The common and intimate association of gypsum with rock salt gives every indication of marine origin, since gypsum or anhydrite, is deposited before the more soluble rock salt. It is also supposed that the action of sulfuric acid, caused by oxidation of sulfides by air and water, on lime and limestone may have been the source of gypsum deposits.

The pure white masses of gypsum known as alabaster very probably received this name from the town Alabastron in Egypt, where ornaments were made from this material in ancient times. Calcined gypsum was used in the construction of the pyramids.

Theophrastus, about 300 B.C., described the occurrence and uses of gypsum, this name being derived from the Greek term applied to calcined gypsum. He states that it was employed as a cement and for casing the outsides of buildings; for making ornaments; and statues; as a color for painters; and for "fulling" cloth. He states - "Gypsum is prepared for use by burning certain stones. It is then reduced to powder and well mixed with water by stirring with wooded instruments. The mixing cannot be done by hand because of the heat developed. This mixture is prepared immediately before it is used, for in a very short time after moistening it dries and becomes hard, and not in condition to be used. The gypsum which has been used can be re-burnt and made fit for use."

Pliny, in his "Historica Naturalis", 77 A.D., described gypsum and noted its close relationship with lime, "cognata calci res gypsum est". This idea was no doubt based on its being prepared as a cement, like lime, by calcining the natural mineral.

Lysistratus of Sicyon is said to have been the first to make plaster casts.

The light transmitted through gypsum plates reminded the ancients of moonlight - hence selenite (transparent gypsum) from the Greek word for the moon.

P. J. Macquer (19) 1747, showed that gypsum contained sulfuric acid, but the mineral was still considered to be unlike CaSO_4 because the former could be converted by calcination into a material which reacted with water, forming a mortar, while the latter remained unaffected by heat.

In 1750, A. S. Marggraf (20) showed that when gypsum and charcoal were heated together, a gas with a pungent odor characteristic of burning sulfur is given off, hence he inferred that it is composed of lime and sulfuric acid. He explains the formation of gypsum in nature by the gradual deposition of the crystals from calcareous waters; time, he said, brings about marvelous results which cannot be duplicated or reproduced in our laboratories.

Lavoisier (21), in 1768, confirmed Margraff's analysis, and showed that the hardening of gypsum is a result of its recombining with the water of crystallization from which it had been deprived by heat. He says - "If the water of hydration removed by fire be returned to it, the water is taken up with avidity, and a sudden and irregular crystallization occurs so that small crystals which are formed become confused with one another and a very hard mass results".

The setting expansion of plaster was known and used by the Persians up to 1880 as a method of executing their criminals.

In 1887, Le Chatelier (22) modified the above somewhat and assumes the mechanism of setting to be - "The hemihydrate first forms a saturated solution in water, then reacts to form the dihydrate giving a supersaturated solution of the latter from which is deposited a compact mass of interlacing needle-shaped crystals - the set plaster".

Since then many scientists have tried to overthrow the above theory in view of colloidal effects during the setting of plaster but Weiser and Moreland, (23) 1932, disprove the colloidal theories and supports that of Le Chatelier.

The dehydration products of gypsum have been studied by Van't Hoff (24), Davis (25) and many others but exact results are lacking due to the various modifications of each hydrate and the difficulty of distinguishing these.

The latest achievement has been that of W. S. Randel and M. C. Dailey (43) relating to the manufacture of a very pure hemihydrate. This process is discussed on page 44

Silica-Plaster Mixtures

The use of silica as a filler in plaster products such as plaster board is probably of recent invention. Its use in plaster moulds dates from 1907 when the method of making metal castings by utilizing a disappearing wax pattern was rediscovered after having been lost to civilization since the time of ancient Egyptians.

The study of the properties of Silica-Plaster mixtures was taken up scientifically at the Bureau of Standards by R. L. Coleman who studied the thermal and setting expansions, porosity and crushing strength of several compositions. The same study was taken up further in 1928 by Coleman (26).

A comprehensive study of the above properties of casting investments consisting principally of plaster and siliceous matter was made by Taylor, Paffenbarger and Sweeney (27). They tested products purchased from the open market and made by various manufacturers. The chemical compositions given include Plaster, insoluble matter (mainly siliceous), Boric Acid and Graphite. By carefully comparing the properties of materials with almost identical compositions it was found that these

properties varied considerably and therefore indicated that what was considered as coloring matter and impurities might be of importance in securing these varying properties.

It was the purpose of this investigation to find the effects of the addition of certain insoluble and soluble materials on the silica-plaster mixtures. The thermal and setting expansions were studied but the tensile strength was determined instead of the compressive strength, as plaster is weaker in tensile strength and would therefore fail first in this property when used for casting moulds. The properties studied are those which are of greatest importance in many of the common uses of plaster and silica mixtures.

CHAPTER III

THEORETICAL

SILICA

One of the most striking facts about silica is the variety of forms in which it occurs. For a long time the relations between these forms or modifications were obscure, and it was not until comparatively recent years that definite information was available concerning them. Even now, our knowledge is by no means satisfactorily complete.

These are eight better-known modifications and their temperature-ranges of stability are as follows:

LOW-QUARTZ (Alpha) - Stable at atmospheric temperatures and up to 573° C.

HIGH-QUARTZ (Beta) - Stable from 573° to 870° ; capable of existence above 870° but is then not the stable form.

LOW-TRIDYMITTE (Alpha) - Capable of existence at atmospheric temperatures and up to 117° , but is not the stable form in this range.

LOWER HIGH-TRIDYMITTE (Beta) - Capable of existence between 117° and 163° , but is not the stable form in this range.

UPPER HIGH-TRIDYMITTE (Gamma) - Capable of existence above 163° , and is the stable form from 870° to 1470° ; above 1470° is again unstable; melts at 1670° .

LOW-CRISTOBALITE (Alpha) - Capable of existence at atmospheric temperatures and up to 200° - 275° , but is not the stable form in this range.

HIGH-CRISTOBALITE (Beta) - Capable of existence above 200° - 275° , and is stable from 1470° to 1710° , its melting point.

VITREOUS SILICA OR SILICA GLASS - Capable of existence at atmospheric temperatures and up to 1000° or above, where it begins to crystallize with measurable rapidity; but is an unstable, undercooled liquid (a glass) at all temperatures below 1710°C.

INVERSIONS OF SILICA - Silica, when heated, undergoes changes or inversions and forms the various modifications shown above. These inversions are reversible upon cooling. There are two types of inversions, a slow or sluggish type and a rapid type called low-high, or alpha-beta type.

The sluggish type of inversion includes those of quartz to tridymite at 870°, tridymite to cristobalite at 1470°, and the melting of cristobalite at 1710°. This type of inversion is characterized by a very slow rate of inversion, it is necessary to hold the substance at a temperature near the inversion temperature for a considerable time, sometimes for days, and often it is necessary to immerse the substance in a molten flux. The inversion proceeds usually from the surfaces of the fragments inward. The modifications differ considerably in physical properties.

The low-high type of inversion (alpha to beta to gamma, and vice versa), sometimes called the "alpha beta", includes those of low quartz (alpha) to high quartz (beta) at 573°, low tridymite to lower high-tridymite at 117°, lower high-tridymite to upper high-tridymite at 163°, and low cristobalite to high-cristobalite at 200-275°. This high-low type is characterized by a very rapid rate of inversion. The change occurs as soon as the temperature is

reached, a flux is never needed. The inversion takes place throughout the whole crystal and does not proceed gradually from the surface inward. The substance cannot be heated or cooled far past the inversion point without undergoing the change as is the case with the sluggish type. The modifications of this type do not differ greatly in physical properties.

The principal property that we are interested in in this investigation with regard to silica is the thermal expansion. Some of the most exacting measurements on the linear thermal expansion of the various modifications are given in curves 1 to 5. The dilatation of various samples may vary somewhat. Samples prepared through the sluggish inversions are known to vary considerably as shown in figure (4) on cristobalite.

RELATION OF SPECIFIC VOLUME TO INVERSION TEMPERATURE (28) -

The relation between the temperature of the inversion point and the specific volume at the inversion point for quartz, tridymite, and cristobalite, using the lowest values for the inversion of the two latter forms may be expressed thus:

$$V = 488 - .11T \quad V = \text{Kilo volume}$$

$$T = \text{absolute temp. } ^\circ\text{C.}$$

The calculated values as shown before are in agreement with the observed:

	<u>T</u>	<u>V(calc)</u>	<u>V(obs)</u>
Quartz	846	395	395
Tridymite	390	445	445
Cristobalite	473	436	436

THEORY OF THERMAL DILATATION OF SILICA (29) - The thermal changes in volume and shape of silica may be looked upon as made up of three effects:

(1). The normal thermal dilatation observed in any aggregate of molecules, by which their average distance apart is increased when their thermal vibration increases with rising temperature.

(2). The change which takes place in the distance between two atoms accompanying that change in their relative position which culminates in the high-low inversion. A distinctive feature of this expansion is its logarithmic increase with temperature up to the final abrupt change.

(3). The gradual shrinkage in volume of some unit of structure, possibly the SiO_2 atom triplet, when certain pairs of atoms are in the high temperature position and the temperature is rising.

QUARTZ (CURVES NOS. 1 and 2) - Effect one is subordinate in quartz. The expansion curve of low quartz consists mainly of effect two, the building up toward the inversion at 573° followed above 573° by effect three the thermal shrinkage of the high configuration.

The form of the quartz curve is not that which would result from the presence of two molecular species in equilibrium, of which one is increasing in concentration at the expense of the other. It is rather the form of curve which would result from the action of opposing mechanical forces.

"Various mechanical models of such a system will suggest themselves. For example, the curve showing the relation between the angular velocity and the momentum of the forces on two co-axial cylinders rotating in water has a discontinuity like that in the quartz curve, since there is a limiting value of the velocity below which the momentum is proportional to the velocity, and above which the square of the velocity enters".

TRIDYMITTE (CURVE NO. 3) - The low-temperature expansion of Tridymite is unknown at present but is more than likely a normal thermal dilatation. The position of the oxygen atoms of low-tridymite already approximates to the high-temperature configuration, and the volume-changes at the inversion are small. At higher temperatures the shrinkage effect (effect three) becomes the most important and the volume tends toward constancy and may decrease. As the melting point is approached we may expect the expansion

coefficient to tend toward a positive value again.

CRISTOBALITE (CURVE NO. 4) - The inter-atomic distances in cristobalite are variable, and its high-low inversion is therefore spread over a range of temperature, giving a doubly rounded form to the volume-temperature curve. At higher temperatures it is like tridymite in reaching constancy or a maximum and would probably increase again if followed to a high enough temperature.

VITREOUS SILICA (CURVE NO. 5) - According to the theory (30) liquid silica is a tangle of silica threads. We thus have superposed on the structure of the atom-triplet SiO_2 , another structure, though not a regular or symmetrical one. This structure is partly preserved by the rapid cooling which leads to the formation of a glass. Hence many of the interconnections of oxygen and silicon atoms are of the high temperature configuration, even at temperatures near absolute zero. The principal results of this structure are: first, a negligible amount of thermal dilatation of the normal type; and, second, a shrinkage beginning at very low temperatures.

PHENOMINA OF THE INVERSIONS (HIGH-LOW) - Some of the most important changes involved at the inversion of quartz include sharp change in the thermal dilatation, change in optical rotating power, time-temperature curve (31) shows an absorption of heat due to the inversion, and

changes in refraction index. Upon cooling these changes in volume and shape and optical properties are reversed.

The phenomena of the inversions are also to be found in several compounds containing silica such as glasses, feldspar, calcium and magnesium metasilicates.

CURVE NO. 1

~ LINEAR EXPANSION OF QUARTZ ~

— PARALLEL TO AXIS

--- PERPENDICULAR TO AXIS

(KOZU & SAIKI 33)

PERCENT EXPANSION

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0

0 200 400 600 800 1000 1200 1400 1600 °F
0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CURVE NO. 2

LINEAR EXPANSION OF QUARTZ AGGREGATES

— AGGLOMERATED QUARTZ

— GRÈS GANISTER

} BRAISCO (48)

PERCENT EXPANSION

16
14
12
10
8
6
4
2
0

0 200 400 600 800 1000 1200 1400 1600 °F

0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CURVE NO. 3

~ LINEAR EXPANSION OF TRIDYMITITE AGGREGATE ~

BRAESCO (18)

PERCENT EXPANSION

18
16
14
12
10
8
6
4
2
0
0 200 400 600 800 1000 1200 1400 1600 °F
0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CURVE NO. 2

~ LINEAR EXPANSION OF CRISTOBALITE AGGREGATES ~

BRAESCO { MADE AT 1100°C ---
 (48) { MADE AT 1400°C ---
 { MADE AT 1600°C ---

SWEENEY { SAMPLE NO. 17 ---
 (49) { SAMPLE NO. 13 ---

PERCENT EXPANSION

2.0

1.8

1.6

1.4

1.2

1.0

0.8

0.6

0.4

0.2

0

0

200

400

600

800

1000

1200

1400

1600 °F

0

100

200

300

400

500

600

700

800 °C

TEMPERATURE

CURVE NO. 5

~ LINEAR EXPANSION OF FUSED QUARTZ ~
SOUDEK & HIGNERT (45)

PERCENT EXPANSION

0.0
0.1
0.2
0.3
0.4
0.5

0 200 400 600 800 1000 1200 1400 1600 1800 °F
0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CHEMICAL PROPERTIES - We are not too well informed on the action of silica in combination with plaster and other ingredients at high temperatures but it is fairly safe to assume that the silica acts more or less as an inert filler. It is known that silica in contact with water does form some silicic acid on the surface the amount depending on: fineness of subdivision, time temperature and pressure.

This fact, however, is important since silica is found most useful as a filler or aggregate in cements, concretes, and plaster. The hard sharp grains seem to be cemented in place by this surface effect and adds to the stability of the mass when dry and hardened.

HYDRATES OF CALCIUM SULPHATE - The following table lists the chief crystallographic characteristics of the three hydrates (32) and other properties:

	<u>Gypsum</u> ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)	<u>Hemihydrate</u> ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$)	<u>Anhydrite</u> (CaSO_4)
System & Habit	Biaxial Positive Monoclinic	Uniaxial Positive Trigonal	Biaxial Positive Orthorhombic
Index of Refraction			
alpha	1.520	No 1.55	1.571
beta	1.523	----	1.576
gamma	1.530	No 1.57	1.614
Hardness	1.5-2	----	3.00
Specific Gravity	2.32	2.78	2.93
Percent Water	20.91	6.20	----

Soluble anhydrite, which may be formed by dehydrating gypsum or hemihydrate in air at a temperature not in excess of 250-300°C., is according to the latest school of thought, purely dehydrated hemihydrate and is identical with the latter as to crystal form. Water of crystallization contained in hemihydrate is now thought to be seelitically combined.

The conversion of one form into another by heating and the temperature at which this occurs has been determined by H. Le Chatelier (22). The time-temperature curve is shown in curve number (6) and shows a rise of temperature to 128°, a long interval of no change, a steady rise between 128° and 163°, a second but shorter interval of no change

and another rise. There was a continuous loss of weight on heating gypsum to 155° until 15.6% had been lost leaving a residue which remained at a constant weight corresponding with the hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$); similarly the loss in weight at 194° was continuous until the anhydrous sulfate was formed, then a residue of constant weight remains.

Curve number (7) shows the vapor pressures of the various systems of hydrates of CaSO_4 and water according to Van't Hoff and Armstrong (34). The transition points are shown (intersection of curves with curve of pure water); that is, when gypsum is heated with water under pressure, above 107° , the hemihydrate will be formed, and when the latter is heated with water below 107° , gypsum will be formed. The transition temperature is lowered in the presence of solutions having a vapor pressure lower than that of water and will occur at the temperature at which the vapor pressure of the system $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ becomes equal to the vapor pressure of the solution.

W. A. Davis (25) says that upon dehydration monoclinic gypsum first reverts to the rhombic form and the reverse is true upon rehydration. The changes are reversible

These changes are true in the setting of plaster, for a time after the material is hard the orthorhombic dihydrate is produced, after a time the stable monoclinic gypsum is formed.

Various authors have shown that the formation of the various hydrates may occur at various temperatures depending upon the rate of heating and condition of the air or liquid in which the product is heated; thus, gypsum was completely dehydrated at 70° in a stream of dry air but formed the hemihydrate at 100° in ordinary (undried) air. While the hemihydrate does not lose water in the air at 98° it gives the soluble anhydrite when heated for nine hours in toluene at 107°, Gypsum may be entirely converted to the soluble anhydrite at 145° in 4 hours.

Soluble anhydrite is extremely hygroscopic and will revert to the hemihydrate upon exposure to the air. It will then mechanically retain up to 2% moisture varying with the humidity of the air.

M. Glasenapp (35) states that at a red heat some basic sulfate is formed ($\text{CaSO}_4 \cdot \text{CaO}$).

A. L. Keane (36) found that when gypsum is calcined at 600° and ground to a particle size of .05 mm. diameter, it behaved like ordinary dead burnt plaster (natural anhydrite) but when reduced to a particle size of one-tenth this diameter, it set quite rapidly.

CURVE NO. 6

HEATING CURVE OF GYPSUM

(H. LE CHATELIER (18))

CURVE NO. 7

~ VAPOR PRESSURE OF CaSO_4 HYDRATES AND H_2O ~

(VANT HOFF (34))

VAPOR PRESSURE IN MM

1200
1100
1000
900
800
700
600
500
400
300
200
100
0

— H_2O
 --- $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} - \text{H}_2\text{O}$
 — $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{CaSO}_4$ (SOLUBLE ANHYDRITE) — H_2O
 — $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{CaSO}_4$ (NATURAL ANHYDRITE) — H_2O

20 30 40 50 60 70 80 90 100 110

TEMPERATURE IN $^{\circ}\text{C}$.

SETTING EXPANSION OF PLASTER - The fact that plaster expands on setting has been known for many years. R. J. Friswell (37) reports that the setting expansion of plaster was utilized in Persia for executing criminals up to fairly recent times (about 1880). The subject was placed in hollow stone columns and surrounded with wet plaster.

The utility of plaster in making moulds depends greatly on its setting expansion by which property it fills the mould and penetrates into every corner, thus taking a sharp impression.

The setting expansion of plaster is only apparent since the volume of set plaster is less than the combined volumes of plaster and water before mixing. If the reaction be represented by the equations $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 1\frac{1}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ the contraction is close to 7% (cubic).

W. A. Davis (25) interprets the mechanism of setting expansion as a preliminary contraction due to reaction with water forming the rhombic form of gypsum, and the subsequent expansion as a result of the change to the monoclinic form of gypsum.

G. P. Grimsley (38) states that the setting expansion is due to the outward thrust of the crystals in the direction of their growth.

Since heat is required to dehydrate plaster, heat is in turn given up upon rehydration, this may amount to as much as 20°C. Some attribute the heating of the plaster as causing the setting expansion but this may amount to .6% which is more than ten times the thermal expansion in this range.

THE SETTING OF PLASTER OF PARIS - Le Chatelier (22) explained the mechanism for the setting of plaster as follows - "The hemihydrate first forms a saturated solution in water, then reacts to form the dihydrate giving a supersaturated solution of the latter from which is deposited a compact interlacing needle-shaped crystals - the set plaster".

For a number of years this theory was considered adequate until W. Michaelis (29) and Keisermann (40) observed the formation of a jelly as well as of crystals in the setting of Portland cement, they have therefore visualized the formation of a jelly as an intermediate stage in the setting of plaster. For a discussion of these theories the reader is referred to Weiser and Moreland (23).

Since the setting of plaster is an exothermic reaction the time required to attain the maximum temperature has been used to determine the setting time of plaster by Weiser and Moreland (23) from whose article the following discussion and data are taken.

The addition of small amounts of gypsum (set plaster) to the hemihydrate (plaster) either to the solid or in the water with which it is mixed accelerates the setting time of plaster. Practically 100% plaster set in 100 min., while the addition of 1% gypsum decreased this time to 14 minutes.

A typical time-temperature curve for Plaster of Paris seeded with gypsum is shown in curve number 8. The curve of plaster alone shows a sharp rise of approximately 1°C , which is due to the heat of transformation of any anhydrate to hemihydrate. This initial rise is followed by a "period of inhibition" after which there is a steady increase in temperature until the maximum is attained, a steady decrease follows.

The shapes of the curves indicate that the length of the inhibition period is greatly controlled by the amount of gypsum nuclei in the paste after mixing with water is complete. The observed inhibition period appears to result from the delayed precipitation from a supersaturated solution owing to a dearth of nuclei.

The period of inhibition is not a period of rest, chemically, for there is a gradual but continuous precipitation of more and more gypsum on nuclei present until there is rapid precipitation of gypsum followed by further solution and hydration of hemihydrate throughout the mass. The initial temperature standstill is due to loss of heat from evaporation of excess surface water or improper insulation of apparatus.

Since the increase in viscosity of the plaster paste is gradual, it is impossible to designate any one place where the initial set takes place, this is measured by some arbitrary test such as the Vicat apparatus.

CURVE NO. 8

EFFECT OF GYPSUM ON TIME-TEMP. CURVE OF PLASTER
(WEISER AND MORLAND 1933)

EFFECT OF ELECTROLYTES ON THE SETTING OF PLASTER (23) -

Since the setting of plaster involves the precipitation of gypsum from its supersaturated solution, the effect of electrolytes on the process may be considered in the light of von Weimarn's theory of the precipitation process (41).

Von Weimarn considers the following as the most important factors on which precipitation depends --

- (1) The solubility of the precipitation substance.
- (2) Concentration at which precipitation begins.

The process of precipitation takes place in two stages.

- (1) The molecules first condense to invisible or ultra-microscopic particles.
- (2) The growth of the particles as the result of diffusion.

In stage (1) the velocity W at the first moment can be formulated.

$$W = K \frac{\text{precipitation pressure}}{\text{precipitation resistance}} = K \frac{Q-L}{L} = K \frac{P}{L} = KU$$

K = a constant

Q = total concentration of substance that is to precipitate

L = solubility of the substance

$Q-L$ = amount of supersaturation = P

$P-U$ = % supersaturation

L

In case of a large value of P a large amount of precipitate will be thrown down in a certain time. If L is small a relatively small amount of precipitate will form.

The velocity V of the second stage of the process is given by the Harnst-Noyes equation

$$V = D/S \cdot O \cdot (Q - L)$$

where D is the diffusion coefficient, S the length of the diffusion path, O the surface, Q the concentration of the surrounding solution and L the solubility of the dispersed phase for a given degree of dispersity. As in the von Weimarn equation $Q - L$ is the absolute supersaturation.

This general statement of the conditions which occur during precipitation from solution may now be applied to the precipitation of gypsum from its solution both in the presence and in the absence of foreign electrolytes. The solubility of plaster of Paris in water is approximately 0.067 mol per liter (42) and when this hydrates to gypsum which has a solubility of but 0.015 mol per liter, the percentage supersaturation is $\frac{0.067 - 0.015}{0.015} = 3.5 = U$. The initial velocity of precipitation is proportional to U , that is, $W = 3.5 K$. In view of the relatively long period of inhibition following the mixing of pure plaster of Paris with water, it is obvious that this percentage supersaturation is insufficient to cause rapid precipitation of nuclei which must be present in abundance for a rapid reaction to take place throughout the mass. Now if the addition of a foreign electrolyte cuts down the period of inhibition it follows that the percentage supersaturation of the solution with respect to gypsum must be greatly increased. This may be accomplished in one of two ways: Either the solubility of

the hemihydrate is increased appreciably more than that of hemihydrate by the presence of the foreign electrolyte. In the first instance the value of $(Q-L)/L = P/L$, the percentage supersaturation, is increased because the value of Q , which is determined by the solubility of hemihydrate is increased proportionately more than L the solubility of the gypsum in the medium; and in the second case P/L is increased because L is decreased proportionately more than P in the give medium. In other words for a foreign electrolyte to change the initial rate of formation of nuclei as compared to the rate of formation in water alone, all that is necessary, other things being equal, is for the ratio of solubility of hemihydrate to the solubility of gypsum to be greater or less than 4.5, the ratio of the solubilities in pure water.

EFFECT OF AMMONIUM NITRATE (A TYPICAL ACCELERATOR) (23) -

"The time-temperature curves of the setting of plaster upon addition of varying amounts of ammonium nitrate (curve number 9) are similar to those of the addition of gypsum (curve number 8). The solubility curve of gypsum in ammonium nitrate solution is given in curve No. 9. The U-shaped form of the rate of set curve indicates that with low concentrations of nitrate solution, the ratio of the solubility of hemihydrate to gypsum is sufficiently large that a high percentage supersaturation of gypsum obtains. This results in prompt precipitation of nuclei and because of relatively high absolute supersaturation the growth of the crystals

goes on rapidly until the reaction is complete. On the other hand, in strong nitrate solution in which gypsum is quite soluble, $Q - L = P$ is small and P/L is small so that the initial formation of nuclei and the subsequent growth of crystals is greatly retarded.

The form of the gypsum crystals in the set plaster is influenced in great measure by the factors determining the absolute supersaturation and the number of nuclei. If L is small so that the $Q - L$ value is relatively large, the crystals grow very rapidly and are not well formed; while if L is large so that $Q - L$ is relatively small, large well-formed crystals result, provided the plaster is not seeded with gypsum nuclei.

The above deductions have been confirmed by extended thermometric and microscopic observations on the setting of plaster of Paris in solutions of varying concentrations of NH_4NO_3 , NH_4Cl , NH_4CNS , $(\text{NH}_4)_2\text{SO}_4$, NaCl and MgCl_2 . Curve number 10 shows effects of varying concentrations of the latter salts on the rate of set of plaster.

Contrary to what would be predicted from von Weimarn's theory the rate of set of plaster of Paris in dilute ammonium acetate solutions is much slower than would be expected from solubility relations and the prevailing supersaturation. The reason for the retarding action of ammonium acetate is that gypsum does not deposit readily from its supersaturated solution on gypsum nuclei formed in the presence of ammonium acetate probably because

of an absorbed film of acetate on all the surfaces of the crystals. The addition of gypsum nuclei formed in the absence of acetate, induce a rapid rate of set.

The effect of such salts as ammonium acetate and ammonium citrate on the rate of set of plaster of Paris is similar to that of small amounts of glue and gelatin, the absorption of which on the gypsum nuclei inhibits or prevents the growth of the crystals and so delays or prevents the setting of the plaster.

X-radiograms of the widely different forms of crystals obtained by the actions of plaster in solutions of the several electrolytes, disclose that the crystals are identical in structure with gypsum formed in the presence of H_2O alone."

CURVE NO. 9

EFFECT OF THE CONCENTRATION OF NH_4NO_3

ON THE RATE OF SET OF PLASTER

(WEISER AND MORELAND (23))

CURVE NO. 10

~ EFFECT OF VARYING CONCENTRATIONS OF
SEVERAL ELECTROLYTES ON
THE RATE OF SET OF PLASTER OF PARIS ~
(WEISER & MORELAND (23))

MANUFACTURE OF PLASTER - To make plaster, gypsum is heated to a temperature above which dehydration occurs and this water must be removed or it will recombine. The following reaction occurs:

The product is known as hemihydrate, calcined gypsum, first settle stucco, and plaster.

Products made by calcining to a higher temperature include CaSO_4 made between 130 and 525°C known as soluble anhydrite or second settle stucco; CaSO_4 made slightly above 525°C, known as flooring plaster and sets very slowly; CaSO_4 made above 600°C and known as "dead burned" sets extremely slow.

For a detailed description of apparatus, plants, and methods of making plaster the reader is referred to "The Technology of Manufacture of Gypsum Products", Circular of the Bureau of Standards No. 281.

While the theoretical temperature at which gypsum forms plaster is 107°C for a saturated air, the practical method utilizes temperatures varying from 149°C (300°F) to 177°C (350°F). These temperatures are measured at the tops of the kettles near the top of the batch. These high temperatures rather than the theoretical one has been found necessary for volume production. Under these conditions however, there are other hydrates formed as well as some unconverted gypsum which changes the setting properties of plaster on aging.

W. S. Randel and M. C. Dailey (43) have shown that in the above processes as carried out, heat in large quantities is suddenly applied to the gypsum crystals. This sudden application changes the liberated water to steam which literally explodes the gypsum crystals into very minute plaster crystals. The latter are so small that only recently has it been established that the plaster is crystalline. The prior thought that it was amorphous was due to the inability of petrographic microscopists to see the crystals because of the extreme fineness and spongy characters of the plaster.

They have discovered that by applying heat to gypsum under definite control of temperature, time, and pressure a form of plaster is made which is definitely crystalline. This product they designate as "alpha-gypsum," it is substantially monomineralic, and when ground consists of cleavage fragments and crystals of pure hemihydrate in the form of short rods or prisms. It differs from plaster in being free from unchanged gypsum and therefore a uniform product. It is denser than plaster and requires less water to form a paste of the same consistency. It also gives a much denser and stronger product and does not require long periods of aging. The thermal expansion of mixtures with silica is greater than with an equal proportion of silica and plaster.

THERMAL EXPANSION - Thermal expansion is the change in dimensions of a substance due to heating. This has been found to be a property of a substance just as its density or refractive index and differs with different materials. The difference in expansion of materials of crystalline nature along their different axes of symmetry have been studied by Fizeau (44) and is shown in Table I, Appendix.

A convenient method of comparing the dilatation of various substances is the expansion per unit volume. The latter may be expressed as

$$a_0 = \frac{1}{v_0} \cdot \frac{dv}{dt}$$

a_0 = coefficient of expansion (cubical)

v_0 = volume of one gram at 0°C. (or any starting temperature)

dv = change in volume of one gram of substance

dt = change in temperature (in degrees)

Linear expansion is given by the expression

$$a_L = \frac{1}{L_0} \cdot \frac{L - L_0}{t - t_0}$$

a_L = mean linear coefficient of expansion

L_0 = initial length of substance

L = final length of substance

t_0 = initial temperature of test

t = final temperature of test

The simplest and fairly exact expression is

$$L = L_0 (1 + a_L t) \quad L = \text{final length}$$

$L_0 = \text{initial length}$

$a_L = \text{mean linear coefficient of expansion}$

$t = \text{change in temperature during test}$

For an isotropic substance

$$a_0 = 3a_L \text{ (very nearly)} \quad a_0 = \text{mean coefficient of expansion (cubical)}$$

$a_L = \text{mean coefficient of expansion (linear)}$

For an anisotropic substance (such as quartz)

$$a_0 = a_{L\parallel} + 2a_{L\perp} \quad a_0 = \text{mean coefficient of expansion (cubical)}$$

$a_{L\parallel} = \text{mean coefficient of expansion (linear) parallel to principal axis, or axial coefficient}$

$a_{L\perp} = \text{mean coefficient of expansion perpendicular to principal axis or equatorial coefficient}$

or

$$a_L \text{ (average)} = \frac{a_{L\parallel} + 2a_{L\perp}}{3} \quad a_L = \text{mean linear coefficient of expansion}$$

Percent linear expansion =

$$\frac{(a_L) (t_1 - t_2)}{L_0} \times 100$$

a_L = mean linear coefficient
of expansion

t_1 = initial temperature of
test

t_2 = final temperature of test

L_0 = original length of specimen

All of the experimental data will be given in percent linear expansion as this has been found to be the best and most convenient method of presenting this particular type of data.

In table I, Appendix, are shown the coefficients of expansion of various materials belonging to the several crystallographic systems. These data show the differences in expansion along the various axes of the same crystals.

Table II, Appendix, gives the linear coefficient of expansion of many minerals, refractories, and salts, some of which will be studied in this investigation.

THE MEASURING OF THERMAL EXPANSION - Since the development of the Interferometric method for measuring thermal expansion by H. Fizeau (7) there have been many new types of apparatus developed which are more convenient for specific uses. For a selected bibliography of expansion apparatus, the reader is referred to Souder and Hidnert (45). To the

latter list may be added a description of the latest apparatus of the Interferometer type by G. E. Merrit (46) and an Autographic apparatus by Souder, Hidnert, and Fox (47). The fused-quartz tube method will be described in detail in the section entitled apparatus.

There are two methods in general use for measuring expansion, one is the equilibrium and another the mobile. When using the equilibrium method the specimen is held for a sufficient length of time at each temperature where measurements are taken until equilibrium conditions are reached; this sometimes requires several hours at each temperature.

Another method known as the mobile method is used for materials whose expansion follows the increase in temperature in a regular way and an approximate value for the expansion under equilibrium conditions may be obtained by heating the sample continuously at a slow rate.

True thermal expansion is to be obtained only in materials where the increase in size results from an increase in effective size of the constituent molecules without any change in their relative arrangement. In some materials the rearrangement of the molecules into different configurations may be very rapid, such as the quick inversion of the various forms of silica. In other cases the changes may be very slow such as in the annealing of glass.

In either of the above cases the quick changes will be lost or neglected by the equilibrium method and therefore the continuous or mobile method is more useful for such materials. Whereas this method is not as exact for absolute measurement of expansion it gives other information that is very useful. The choice of method therefore depends on the purpose in view. The equilibrium values are given most frequently in the literature.

In this investigation the mobile method is used exclusively for the following reasons: silica is used in most samples, comparative results are desired, the substances are heated rapidly in actual use. A comparison with some values made by the equilibrium method will be made.

CHAPTER IV

MATERIALS

MATERIALS - The following is a description of the materials, their properties, with a number designating the sample in which each was used.

SILICA - This term as used in this investigation refers to a material ground from quartz of the following analysis:

SiO_2	99.81%
Al_2O_3	.17%
Fe_2O_3	.014%
CaO	None
MgO	None
Other impurities ..	.006%

and ground so that 99.98% passed the 100 mesh screen and 98.6% passed the 325 mesh screen, except in the case of samples 23 and 24 which were ground so that 93.89 and 78.60 percent, respectively, passed through the 325 mesh screen. The silica was of the same composition chemically.

PLASTER - The plaster used in all runs except No's 47, 48, and 49, was manufactured by the United States Gypsum Co., under patent No. 1,901,051. It is known as "alpha - gypsum" or hydrocal.

It is made from a gypsum base of the following analysis:

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	95.36%
CaSO_4	4.20%
SiO_2 Insol	.14%
R_2O_3 MgO	Trace
CO_2	Trace to .20%

Specifications on the hydrocal are as follows:

Consistency..... 38 to 42 (cc. of water to
100 grams of Hydrocal)
Gilmore set (initial)..... 7 to 12 minutes
Gilmore set (final).....
Compressive strength (dry)... 6,000 to 8,500 lbs.
per sq. in.
Tensile strength (dry)..... 550 to 900 lbs. per
sq. in.
Grind..... 99% minimum thru 100 mesh
Expansion (setting)..... .32 to .45%

The plaster used in runs 47, 48 and 49 was ordinary plaster made by the kettle process. Its grind and purity is the same as the hydrocal but it sets slower and is weaker in compressive and tensile strengths.

RETARDER - A retarder was used to adjust the setting time of the various samples. The retarder used is produced commercially and is known as "sodate". Its composition has not been made public by the manufacturer. It is most probably an organic salt in an inert carrier.

WATER - To insure uniformity distilled water was used. It was stored in a large bottle and maintained at room temperature.

TITANIUM OXIDE (Sample No. 16) - The titanium oxide was of the type used as a paint pigment.

SODIUM SILICATE (SAMPLES NO'S 17 and 29) - The sodium silicate was a dry form manufactured by the Philadelphia Quartz Co., grade SS - 20, ground to pass 100 mesh for sample No. 17; for sample No. 29, the material was ground to pass 200 mesh.

CALCIUM FLUORIDE (SAMPLE NO. 18) - The calcium fluoride was very finely pulverized fluerspar.

ZINC OXIDE (SAMPLE NO. 19) - C. P. zinc oxide was used; about 300 mesh.

BORIC ACID (SAMPLE NO. 20) - A very good grade of commercial boric acid was used, finely powdered.

POTASSIUM SULFATE (SAMPLE NO. 21) - The N. F. grade of potassium sulfate was used as an accelerator in sample No. 21.

CHROMIC OXIDE (SAMPLES NO'S 25 and 26) - A technical grade of Cr_2O_3 was used, about 150 mesh.

CRISTOBALITE (SAMPLES NO'S 27 and 33) - The cristobalite used in sample No. 33 showed about 60 to 70% cristobalite, 30 to 40% tridymite, upon petrographic analysis. It was most probably made by long heating of about 1200°C .

For sample No. 27 a well converted product was used, petrographic analysis showed most of it to have a refractive index of 1.484 to 1.487, a small amount of quartz was present. Both samples were 300 mesh and finer.

LITHIUM CARBONATE (SAMPLES NO'S 28, 31 and 32) - A commercial grade was used, ground to pass 200 mesh entirely.

BERYL (SAMPLE NO. 30) - A commercial grade of beryl as used for enamel manufacture was used. It was about 150 mesh.

CALCIUM SILICATE (SAMPLE NO. 34) - The calcium silicate was a C. P. grade, about 300 mesh.

VERMICULITE (SAMPLES NO'S 35, 36 and 45) - The vermiculite was a fairly pure commercial product ground to 300 mesh.

ALUMINUM OXIDE - The aluminum oxide was electrically fused and somewhat colored by impurities. Analysis as follows:

Al_2O_3	96.%
SiO_2	1.%
TiO_2	2.%
Fe_2O_3	0.3%
Cr_2O_3 MgO.....	---

Sp. Gravity = 3.96, fusion temp. = $1750^\circ - 2000^\circ\text{C}$.

CHROMITE - The chrome ore used had the following analysis (approx.)

Al_2O_3	30.%
SiO_2	5.%
Cr_2O_3	35.%
MgO.....	15.%
Fe_2O_3	15.%

Sp. Gravity = 3.95.

BARIUM SULFATE (SAMPLE NO. 39) - A technical grade of barium sulfate was used, about 200 mesh.

FELDSPAR (SAMPLE NO. 40) - A potash feldspar was used,
300 mesh.

METRONITE (SAMPLE NO. 41) - Metronite, 100% thru 325 mesh,
analysis as follows:

Calcium Magnesium Carbonite....	65.7%
Calcium Magnesium Silicate.....	34.2%
Moisture.....	.1%

ANHYDRITE (CaSO_4) (SAMPLES NO'S 42 and 43) - The anhydrite (CaSO_4) for sample No. 42 was about 100 mesh. The anhydrite (CaSO_4) for sample No. 43 was about 200 mesh. The anhydrite was a naturally occurring mineral from Oklahoma.

WOLLASTONITE (SAMPLE NO. 44) - The wollastonite used was a natural mineral ground to pass 200 mesh screen.

MAGNESIUM OXIDE (SAMPLE NO. 46) - A commercial electrically fused very dense MgO , ground to 200 mesh was used.

GYPSUM (SAMPLE NO. 50) - A commercial grade, about 150 mesh, known as "land plaster" was used. It was from Oklahoma and was of the same analysis as the plaster used.

CHAPTER V

APPARATUS

APPARATUS

I. THERMAL EXPANSION DILATOMETER - In Fig. (1) is shown the thermal expansion equipment. From left to right are shown the Portable Potentiometer Indicator, Fused Quartz Tube Dilatometer Complete, Rheostat and Coil Device for regulating the current, and an additional furnace.

The Fused Quartz Tube Dilatometer consists of a fused quartz tube and indicating device, and an electrically heated furnace, and a temperature measuring device.

(1) FUSED QUARTZ TUBE - The fused quartz tube is about 20 inches long, closed one inch from the bottom, and $3/4$ inch inside diameter. Near the top is attached rigidly an invar device which holds an Ames Dial Gauge of plunger type reading in $1/10,000$ inches. Inside this tube is placed the sample (8 in. long, $1/2$ - $5/8$ in. diameter). On top the sample is placed another closed quartz tube, or movable rod. On this rod the gauge plunger rests. As the sample expands it pushes the movable rod upward and registers on the gauge. Thus the amount read on the gauge is the differential expansion between the sample and an equivalent length of fused quartz. A small correction for the expansion of fused quartz is made from curve No. 5.

(2) FURNACE - The furnaces were exact replicas of that at the National Bureau of Standards and were built from blue prints of the Bureau. In the center of the furnace is a refractory core wound with the heating element and covered with cement. Around the core insulation is packed uniformly

so that there will be practically no temperature gradient between the furnace and the specimen. The furnace is heated by a 110 volt line current of from 1 to 5 amperes, controlled by means of rheostats.

(3) TEMPERATURE MEASURING DEVICE - The temperature was read by means of a direct reading Leeds & Northrup Portable Potentiometer Indicator in which the galvanometer and standard cell are integral parts of the instrument, a room temperature compensator eliminates the need for a specially controlled cold junction.

USES OF THE DILATOMETER - The linear expansion of those solids which can be secured or made into bars 7 to 8 inches long and any diameter up to $5/8$ inches, may be measured in this apparatus from room temperature to 1000°C with an accuracy of 1 to 2 percent. This may be accomplished by either the equilibrium or "mobile" methods. (See page

Data for a time-temperature curve may be secured while determining the thermal expansion. Dehydration, chemical reaction, and inversions may be determined indirectly from the thermal expansion and time-temperature curves.

This type of dilatometer combines good accuracy, ease and speed of operation, ease of preparation and adjustment of samples, wide range of types of specimens, and wide temperature range, better than any other type of thermal expansion equipment.

The accuracy of the instrument is 2 percent or better. In the accompanying letter is given the comparison of the values derived on the dilatometer used (Whip-Mix values) and that of the Bureau of Standards on a sample tested by the latter on the Precision Comparator (45). At low temperatures the values are somewhat in error but at 700°C (1300°F) which is our reference point the error is very small, for this reason the corrections were not included. Identical silica-plaster mixtures gave values differing slightly at low temperatures but differing by less than .1% at 1300°F and above.

II. SETTING EXPANSION APPARATUS - The setting expansion apparatus is shown in Fig. (2). It consists of two micrometer microscopes fastened together rigidly. The expansivity of the base was not included since readings were taken at room temperature within one hour during which time there was very little temperature change.

The sample to be tested was placed on wax paper (to prevent sticking) in the V shaped trough. Reference lines were cut on polished plates and placed in the sample while the latter was still plastic. The distance between the marks was 250 to 260 mm. The percent expansion is taken as the change in length times 100 divided by the original length.

The accuracy of the instrument is given as .005% of the total length.

III. VICAT APPARATUS - A standard Vicat Apparatus (Fig. 2) was used having a 300 gram plunger. The specimen used was one inch in diameter and one inch in height. This size was used rather than the standard A.S.T.M. size for testing plaster and concrete because of the difficulty in mixing the required amount of material in the mixer used. The scarcity and cost of materials in some cases did not permit a large sample. The results are comparative and are not believed to differ from those made on the standard size sample by an amount greater than the accuracy of the test.

IV. MIXER - The dry powders were mixed in a mixer having a screw type propellor revolving on a horizontal axis. This type of mixer has been found to give very uniform mixes.

The powder was mixed with water in a Whip-Mix mechanical spatulator. This type of spatulator consists of a revolving solid blade with a clearance of about .003 inches between this blade and a rubber bowl. The mass is pushed through this small space as the blade revolves. By giving the blade 250 turns (50 turns of the handle) a very uniform and plastic mass is obtained.

V. MOULD - The mould for making the thermal expansion test specimens consisted of an 8 inch tube, 5/8 inch diameter, cut in half along the length. These halves were placed flat on a table and the plastic mass was placed in these, the halves were then placed together and the mass allowed to harden. The halves of the tube were removed, the

specimen out to desired size, a hole for the thermocouple drilled in the center, and the specimen was placed on a shelf to dry for 20 to 24 hours. All specimens were placed in the same place for approximately the same length of time allowed for drying.

VI. SLUMP (CONSISTENCY) APPARATUS (64) - The slump apparatus consisted of a smooth brass tube 2 inches high and 1-3/8 inches inside diameter. It was used to regulate the consistency of the samples as to uniformity. For making a test, 100 grams of powder was mixed with an arbitrary amount of water for 15 seconds, the mix was poured into the tube and at the end of 2 minutes from the time the mixing was begun, the tube was raised slowly and the material allowed to flow out. At the end of another minute the diameter of the bottom of the mass is measured. The consistency used is said to pass the slump test when the average of the maximum and minimum diameters are between 2-1/4 inches and 3 inches. From the first reading an experienced operator can generally regulate the amount of water so that the second test will pass. A third or fourth test is sometimes necessary, however. The $\frac{W}{P}$ values refer to the ratio of water to plaster by weight and were generally those determined by the slump test. Slumps were not run on samples containing less than 10 percent plaster except in the case of samples 15 and 21.

FIG. I

FIG. II

(ABSTRACT OF LETTER)

DEPARTMENT OF COMMERCE
BUREAU OF STANDARDS
WASHINGTON

April 26, 1935

Subject: Thermal Expansion Apparatus

In regard to the set of readings which you now submit for sample 1419 (Dup.), 8 inches long, we desire to state that we obtain the following results from these readings:

Temp. Deg.C.	Gage Reading Inch	Tube Correc- tion Inch	Expan- sion Inch	Percent Expansion Whip-Mix Corp.	Percent Expansion National Bureau of Standards	Percent Error
25	0.0000	0.0000	0.0000	0.000	0.000	---
100	.0098	.0003	.0101	.126	.126	0.0
200	.0228	.0007	.0235	.294	.300	2.0
300	.0363	.0011	.0374	.468	.484	3.3
400	.0520	.0015	.0535	.669	.673	0.6
500	.0676	.0019	.0695	.869	----	---
600	.0834	.0023	.0857	1.071	1.062	.8
700	.0990	.0027	.1017	1.271	1.269	.2
800	.1145	.0031	.1176	1.470	1.476	.4

Respectfully,

H. W. Bearce,
Co-Chief, Division II

CHAPTER VI

EXPERIMENTAL

SAMPLES

The samples were prepared on a weight basis. A pan balance weighing to one tenth gram was used for all weights over 50 grams. Smaller amounts were weighed on a beam balance graduated in $\frac{1}{100}$ gram.

Each of the samples were of 1000 grams except No.'s 15, 21, 22, 23, 24, 26, 27, 33, 41, 42, 43, 45, and 50, these were made up for the particular test only, due to the scarcity of material, or lack of need of large samples because the nature of the material did not permit more than a thermal expansion test.

The samples were mixed for 10 - 20 minutes by 1000 - 1500 turns of the spiral type brush in a dry powder mixer. They were stored in cardboard cans with two lids that insured a good resistance to moisture. These cans were stored in a dry place.

For each test, 50 to 100 grams of the powder was first mixed with the water in a rubber bowl with a spatula until no dry powder remained on the surface. This was followed by 250 turns (50 turns of the handle) in a mechanical spatulator. This insured very good incorporation and reduced entrapped air to a minimum.

All samples except those having less than 10% plaster were adjusted to slump consistency (page) and the $\frac{W}{P}$ (ratio of water to powder by weight) ratio given in

the table is at the slump consistency. All other samples were made with as little water as possible. The composition of samples is given in Table I. Various inert materials were substituted for part of the silica in 10 percent quantities wherever possible. This percentage was kept constant to give comparative results. Materials which were somewhat soluble were used in smaller amounts due to their accelerating or weakening effects.

COMPOSITION OF SAMPLES *

No. No.	W P	% Silica	% Plaster	% (Material)	Sodate
9 1	.42	70.00	30.00		--
11 2	.375	80.00	20.00		--
7 3	.42	60.00	40.00		--
10 4	.35	70.00	30.00		**
12 5	.345	80.00	20.00		**
8 6	.35	60.00	40.00		**
13 7	.34	90.00	10.00		--
5 8	.45	40.00	60.00		--
1 9	.49	-----	100.00		--
3 10	.47	20.00	80.00		--
4 11	.36	20.00	80.00		**
2 12	.37	-----	100.00		**
14 13	.33	90.00	10.00		**
6 14	.35	40.00	60.00		**
17 15	.33	97.00	3.00		--
18 16	.38	60.00	30.00	10.00 Titanium Dioxide	**
38 17	.42	60.00	30.00	10.00 Sodium Silicate	--
39 18	.34	60.00	30.00	10.00 Calcium Fluoride	**
33 19	.49	60.00	30.00	10.00 Zinc Oxide	--
36 20	.35	68.00	30.00	2.00 Boric Acid	--
21	.33	97.00	3.00	.20 Potassium Sulfate	--
22	.33	97.00	3.00		--
16 23	.33	97.00	3.00		--
15 24	.33	97.00	3.00		**
21 25	.35	60.00	30.00	10.00 Chromic Oxide	**

* See Chapter IV.

** Enough to give 15 minutes setting time.

COMPOSITION OF SAMPLES

No.	$\frac{W}{P}$	% Silica	% Plaster	% Material	Sodate
2226	.31	-----	3.00	97.00 Chromic Oxide	--
3027	.35	60.00	30.00	10.00 Cristobalite	**
7728	.36	67.00	30.00	3.00 Lithium Carbonate	--
3729	.41	50.00	30.00	20.00 Sodium Silicate	--
3730	.35	60.00	30.00	10.00 Beryl	**
4531	.34	65.00	30.00	5.00 Lithium Carbonate	--
4332	.38	69.00	30.00	1.00 Lithium Carbonate	--
2933	.35	60.00	30.00	10.00 Cristobalite	**
2334	.40	60.00	30.00	10.00 Calcium Silicate	**
35	.35	69.60	30.00	.35 Vermiculite	**
86	.35	68.43	30.00	1.50 Vermiculite	**
2637	.33	60.00	30.00	10.00 Aluminum Oxide	**
2738	.33	60.00	30.00	10.00 Chromite	**
3539	.33	60.00	30.00	10.00 Barium Sulfate	**
2440	.35	60.00	30.00	10.00 Feldspar	**
1941	.35	60.00	30.00	10.00 Metronite	**
3242	.20	-----	3.00	97.00 Anhydrite	--
3143	.24	-----	3.00	97.00 Anhydrite	--
2544	.35	60.00	30.00	10.00 Wollastonite	**
2045	.35	60.00	30.00	10.00 Vermiculite	**
2846	.35	60.00	30.00	10.00 Magnesium Oxide	**
7247	.36	69.90	30.00	.10 Lithium Fluoride	**
4148	.36	69.80	30.00	.20 Lithium Fluoride	**
4049	.36	69.00	30.00	1.00 Lithium Fluoride	**
50	.26	-----	3.00	97.00 Gypsum	--

PROCEDURE

THERMAL EXPANSION TESTS - The thermal expansion of the 50 samples was determined, values are given in Table II, and the data is plotted in curves (11 to 41).

Readings were taken at room temperature (Approx. 70°F.), at 100°F, and thereafter the readings were obtained at 50°F intervals. The temperature was allowed to rise at the rate of 7 to 8°F per minute until the inversion of silica had occurred. From this point (1100°F) to 1500°F the full current was turned on and the specimen was heated at the rate of 20°F per minute. This more rapid rise in temperature gave results which were identical with a slower rate of heating in several cases, also the heat penetrates more evenly at these temperatures of red heat.

The reference temperature of 1200°F is used as this is the mould temperature specified by most manufacturers of investments for casting of metals (generally precious).

The silica-plaster system was investigated in two series. In the first series only plaster and silica was used and the water ratio adjusted accordingly. Since the virgin plaster begins to thicken while making the slump test, those samples containing a high percentage of plaster required a large amount of water. Another series was made with the setting time of the samples adjusted to 15 minutes by the addition of retarder (sodate). Generally .03 to .1% of sodate gave the required setting time, the higher the percentage of plaster the greater the amount of sodate needed.

The silica-plaster system having been completed, it was found that the 30% plaster, 70% silica is the best for combining fair strength with high thermal expansion. Having selected this composition it was decided to try the effects of the addition of other materials in place of some of the silica while keeping the plaster constant and adjusting the setting time to 15 minutes.

SETTING EXPANSION TESTS - The setting expansion of the various silica-plaster mixtures were found. The effects of the other added ingredients were also studied. Where several percentages of the same ingredients were tried only that containing the highest percentage was tested, as this would demonstrate the effect to the greatest extent.

SETTING TIME - Only the pure silica-plaster mixtures were tested for setting time as all the rest were adjusted to 15 minutes sets to keep the $\frac{W}{P}$ ratio nearly constant. Values are given in Table III.

TENSILE STRENGTH - The tensile strength of all specimens except in those cases where several percentages of the same ingredient were tried; in such cases only those samples containing the highest percentage of the added ingredient were tested. Values are given in Table III.

RESULTS OF THERMAL EXPANSION - The results of the thermal expansion tests on silica-plaster mixtures are shown in Table IV and curves 11 to 18.

Curve No. 19 shows the composite results of the thermal expansion tests on the two series of silica-plaster mixtures using only the values at 1300°F.

Curves No.'s 20 to 41, except 26, 37 and 38, show the effect on the thermal expansion of the substitution of other substances for part of the silica.

Curve No. 26 shows the thermal expansion of Chrome Oxide when formed into a specimen using 3% plaster as a binder and mixed with water to form a compact mass.

Curve No. 37 shows the effect of grind on the thermal expansion of Anhydrite.

Curve No. 38 shows the thermal expansion of the various forms of Calcium Sulfate.

RESULTS OF SETTING EXPANSION - The setting expansions of the various samples are given in Table No. III. A composite setting expansion curve for the silica-plaster mixtures was not drawn because a smooth curve could not be drawn through the points.

RESULTS OF SETTING TIME - A composite curve of the setting times of the pure (unretarded) silica-plaster mixtures is given in curve No. 42. The other samples containing over 10% of plaster were adjusted to a 15 minute set.

RESULTS OF TENSILE STRENGTH - The tensile strength of the various samples are given in Table No. III. A composite curve of the silica-plaster system is given in curve No. 43. The results were based on five samples.

Table II Thermal Expansion
Percent Linear Expansion of Samples No.

Temp. °F.	1	2	3	4	5
Room	.000%	.000%	.000%	.000%	.000%
100	.024	.018	.025	.024	.033
150	.069	.042	.066	.065	.049
200	.116	.068	.091	.116	.072
250	.153	.063	.120	.155	.105
300	.159	.070	.131	.149	.143
350	.183	.095	.143	.180	.163
400	.186	.120	.150	.184	.193
450	.195	.139	.151	.193	.207
500	.206	.166	.153	.214	.225
550	.178	.183	.081	.220	.229
600	.095	.178	-.071	.190	.230
650	-.014	.139	-.163	.081	.220
700	-.068	.134	-.223	.043	.205
750	-.083	.146	-.269	.036	.210
800	-.084	.170	-.275	.043	.236
850	-.064	.209	-.280	.063	.280
900	-.031	.263	-.255	.100	.325
950	.011	.326	-.201	.171	.396
1000	.071	.409	-.101	.229	.483
1050	.179	.548	.000	.328	.702
1100	.325	.711	.133	.501	.772
1150	.366	.754	.181	.563	.800
1200	.388	.780	.219	.595	.815
1250	.425	.790	.249	.620	.825
1300	.453-	.796-	.273-	.641-	.832-
1350	.481	.805	.294	.663	.843
1400	.520	.814	.318	.685	.849
1450	.539	.818	.339	.713	.852
1500	.563	.820	.350	.738	.854

Table II (cont'd) Thermal Expansion
Percent Linear Expansion of Samples No.

Temp. °F.	6	7	8	9	10
Room	.000%	.000%	.000%	.000%	.000%
100	.026	.019	.031	.058	.053
150	.074	.050	.079	.115	.108
200	.125	.106	.144	.158	.166
250	.155	.155	.156	.114	.131
300	.154	.179	.153	.096	.129
350	.183	.196	.169	.105	.130
400	.182	.200	.176	.074	.109
450	.191	.235	.179	.048	.100
500	.203	.263	.183	.035	.094
550	.199	.290	.153	-.048	.021
600	.144	.300	.104	-.281	-.174
650	.089	.318	-.185	-.820	-.512
700	.040	.323	-.408	-1.188	-.752
750	-.004	.361	-.499	-1.287	-.821
800	-.025	.376	-.500	-1.314	-.830
850	-.023	.425	-.489	-1.320	-.826
900	-.006	.478	-.455	-1.320	-.797
950	.029	.549	-.424	-1.318	-.787
1000	.130	.628	-.374	-1.310	-.770
1050	.239	.754	-.303	-1.308	-.719
1100	.380	.978	-.193	-1.304	-.676
1150	.431	1.028	-.156	-1.260	-.648
1200	.460	1.044	-.129	-1.220	-.612
1250	.483	1.051	-.095	-1.196	-.558
1300	.500	1.058-	-.076	-1.180-	-.542-
1350	.531	1.060	-.030	-1.173	-.494
1400	.555	1.061	-.001	-1.190	-.465
1450	.574	1.061	.036	-1.299	-.427
1500	.575	1.050	.055	-1.500	-.402

Table II(cont'd) Thermal Expansion
Percent Linear Expansion of Samples No.

Temp. °F.	11	12	13	14	15
Room	.000%	.000%	.000%	.000%	.000%
100	.064	.088	.020	.020	.008
150	.086	.117	.048	.064	.024
200	.148	.159	.059	.113	.045
250	.089	.105	.080	.148	.126
300	.085	.094	.096	.141	.149
350	.098	.089	.129	.150	.170
400	.085	.061	.169	.163	.196
450	.078	.035	.201	.151	.224
500	.074	.020	.225	.163	.263
550	.021	-.085	.268	.174	.307
600	-.189	-.259	.285	.104	.353
650	-.533	-.695	.290	-.095	.418
700	-.714	-1.068	.309	-.313	.453
750	-.750	-1.165	.335	-.373	.518
800	-.752	-1.197	.388	-.375	.585
850	-.733	-1.201	.430	-.360	.655
900	-.706	-1.195	.520	-.323	.745
950	-.665	-1.178	.588	-.283	.827
1000	-.625	-1.170	.657	-.218	.904
1050	-.533	-1.150	.813	-.101	1.058
1100	-.490	-1.133	1.002	-.003	1.281
1150	-.451	-1.094	1.050	.058	1.321
1200	-.402	-1.032	1.065	.083	1.337
1250	-.369	-.991	1.070	.105	1.342
1300	-.321-	-.968-	1.073-	.136-	1.343-
1350	-.281	-.950	1.074	.163	1.345
1400	-.245	-.950	1.075	.196	1.339
1450	-.199	-1.020	1.075	.233	1.326
1500	-.175	-1.260	1.076	.267	1.321

Table II (cont'd) Thermal Expansion
Percent Linear Expansion of Samples No.

Temp. °F.	16	17	18	19	20
Room	.000%	.000%	.000%	.000%	.000%
100	.016	.011	.015	.016	.018
150	.066	.049	.051	.060	.058
200	.114	.107	.114	.101	.094
250	.150	.167	.153	.121	.105
300	.160	.172	.135	.149	.129
350	.195	.183	.158	.171	.135
400	.203	.205	.172	.191	.124
450	.215	.214	.174	.219	.126
500	.231	.175	.213	.220	.135
550	.236	.188	.228	.200	.160
600	.158	.198	.224	.040	.194
650	.030	.212	.178	-.145	.221
700	-.133	.216	.112	-.173	.265
750	-.154	.219	.041	-.211	.297
800	-.147	.238	.000	-.216	.333
850	-.115	.282	.004	-.201	.361
900	-.054	.350	.019	-.164	.373
950	-.019	.414	.075	-.124	.390
1000	.040	.493	.138	-.051	.412
1050	.141	.629	.200	.054	.484
1100	.289	.800	.368	.134	.615
1150	.383	.847	.457	.170	.682
1200	.353.	.878	.497	.198	.707
1250	.375	.900	.502	.216	.737
1300	.396-	.912	.506	.219	.755-
1350	.414	.913	.505	.238	.773
1400	.428	.887	.461	.239	.781
1450	.448	.832	.340	.235	.781
1500	1.450	.803	.280	.220	.763

Table II (cont'd) Thermal Expansion
Percent Linear Expansion of Samples No.

Temp. °F.	21	22	23	24	25
Room	.000%	.000%	.000%	.000%	.000%
100	.009	.006	.008	.011	.021
150	.041	.016	.021	.046	.059
200	.085	.052	.038	.084	.096
250	.134	.094	.056	.128	.111
300	.167	.124	.075	.146	.136
350	.191	.153	.118	.151	.160
400	.221	.181	.154	.168	.178
450	.254	.219	.189	.197	.191
500	.303	.256	.232	.242	.208
550	.324	.291	.294	.278	.205
600	.379	.342	.334	.304	.129
650	.425	.405	.379	.374	.005
700	.475	.458	.433	.300	-.059
750	.525	.513	.492	.396	-.063
800	.588	.561	.545	.437	-.044
850	.658	.642	.608	.410	-.024
900	.728	.712	.673	.542	.038
950	.800	.802	.754	.612	.095
1000	.900	.893	.837	.695	.161
1050	1.026	1.038	.987	.832	.275
1100	1.268	1.256	1.205	1.055	.418
1150	1.318	1.309	1.265	1.079	.458
1200	1.335	1.329	1.278	1.082	.488
1250	1.341	1.334	1.279	1.083	.506
1300	1.342-	1.332-	1.280-	1.085-	.524-
1350	1.343	1.333	1.281	1.086	.549
1400	1.345	1.334	1.282	1.083	.565
1450	1.342	1.334	1.280	1.076	.588
1500	1.332	1.331	1.270	1.065	.594

Table II (cont'd) Thermal Expansion
Percent Linear Expansion of Samples No.

Temp. °F.	26	27	28	29	30
Room	.000%	.000%	.000%	.000%	.000%
100	.020	.023	.014	.024	.021
150	.042	.065	.039	.093	.060
200	.070	.110	.066	.171	.104
250	.088	.144	.079	.205	.140
300	.107	.168	.090	.207	.141
350	.130	.205	.096	.222	.168
400	.144	.229	.106	.228	.174
450	.159	.285	.109	.085	.183
500	.183	.329	.134	.044	.206
550	.198	.360	.161	.043	.219
600	.221	.329	.200	.060	.180
650	.242	.236	.238	.084	.118
700	.258	.183	.293	.121	.063
750	.291	.164	.334	.155	.021
800	.308	.166	.383	.196	.019
850	.330	.180	.426	.245	.024
900	.352	.238	.506	.300	.059
950	.372	.281	.576	.361	.101
1000	.392	.340	.657	.434	.165
1050	.415	.446	.779	.582	.284
1100	.440	.589	.925	.706	.410
1150	.460	.639	.951	.750	.464
1200	.479	.663	.956	.783	.484
1250	.500	.680	.954	.792	.504
1300	.520	.693-	.936-	.818-	.524-
1350	.542	.706	.916	.818	.541
1400	.564	.724	.883	.798	.564
1450	.587	.740	.653	.745	.589
1500	.607	.761	.515	.702	.605

Table II (cont'd) Thermal Expansion
Percent Linear Expansion of Samples No.

Temp. °F.	31	32	33	34	35
Room	.000%	.000%	.000%	.000%	.000%
100	.003	.009	.051	.016	.006
150	.006	.025	.061	.053	.044
200	.016	.065	.105	.095	.088
250	.035	.068	.161	.111	.101
300	.053	.074	.150	.108	.119
350	.068	.080	.194	.121	.139
400	.065	.085	.199	.114	.163
450	.059	.105	.214	.124	.173
500	.075	.138	.248	.127	.200
550	.100	.170	.265	.129	.215
600	.126	.201	.219	.067	.179
650	.156	.236	.130	-.043	.051
700	.195	.273	.060	-.058	-.005
750	.230	.306	.056	-.037	-.014
800	.279	.345	.056	-.003	.004
850	.336	.389	.080	.049	.039
900	.398	.443	.113	.085	.088
950	.465	.503	.161	.144	.143
1000	.538	.569	.215	.215	.215
1050	.674	.665	.300	.246	.341
1100	.852	.811	.455	.522	.501
1150	.893	.845	.488	.549	.551
1200	.900	.855	.510	.572	.578
1250	.900	.857	.526	.594	.588
1300	.892-	.857-	.545-	.606-	.601-
1350	.875	.836	.563	.619	.618
1400	.827	.801	.580	.620	.624
1450	.775	.720	.599	.612	.646
1500	.729	.610	.603	.482	.659

Percent Linear Expansion of Samples No.

Temp. °F.	36	37	38	39	40
Room	.000%	.000%	.000%	.000%	.000%
100	.016	.019	.025	.025	.024
150	.064	.064	.069	.068	.063
200	.116	.110	.120	.120	.109
250	.155	.155	.150	.156	.148
300	.156	.165	.166	.183	.161
350	.183	.183	.193	.204	.175
400	.198	.186	.209	.221	.185
450	.215	.200	.228	.236	.198
500	.233	.219	.245	.258	.209
550	.240	.228	.250	.251	.205
600	.204	.210	.208	.171	.143
650	.110	.154	.093	.083	.085
700	.050	.099	.043	.050	.005
750	.039	.034	.015	.048	-.023
800	.039	.010	.018	.053	-.030
850	.054	.011	.038	.080	-.020
900	.103	.040	.078	.118	-.010
950	.156	.080	.129	.166	.064
1000	.223	.155	.190	.232	.113
1050	.329	.264	.330	.329	.190
1100	.498	.405	.455	.501	.361
1150	.555	.455	.508	.548	.406
1200	.576	.491	.534	.580	.446
1250	.598	.513	.555	.595	.475
1300	.615-	.536-	.573-	.636-	.496-
1350	.633	.563	.591	.663	.519
1400	.651	.574	.605	.685	.558
1450	.678	.609	.630	.713	.590
1500	.690	.624	.650	.734	.603

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Table II (cont'd) Thermal Expansion
Percent Linear Expansion of Samples No.

Temp. °F.	41	42	43	44	45
Room	.000	.000	.000	.000	.000
100	.074	.090	.018	.073	.075
150	.064	.056	.058	.061	.068
200	.108	.091	.079	.109	.104
250	.150	.095	.050	.154	.138
300	.156	.070	.014	.153	.111
350	.183	.108	.041	.183	.173
400	.179	.153	.073	.188	.136
450	.188	.180	.103	.195	.143
500	.215	.224	.134	.218	.163
550	.224	.264	.171	.226	.175
600	.196	.291	.199	.201	.149
650	.130	.330	.243	.111	.046
700	.095	.384	.298	.064	.001
750	.084	.434	.331	.043	.001
800	.079	.473	.375	.040	.011
850	.081	.533	.430	.061	.049
900	.104	.586	.480	.096	.089
950	.155	.638	.536	.139	.139
1000	.210	.683	.584	.208	.221
1050	.301	.725	.635	.304	.301
1100	.466	.764	.680	.455	.461
1150	.513	.805	.718	.500	.501
1200	.551	.656	.771	.536	.530
1250	.565	.901	.829	.561	.556
1300	.588-	.955-	.880-	.581-	.580-
1350	.604	1.009	.931	.608	.597
1400	.624	1.055	.976	.629	.613
1450	.626	1.071	.986	.651	.619
1500	.633	1.025	.903	.679	.619

Table II(cont'd) Thermal Expansion
Percent Linear Expansion of Samples No.

Temp. °F.	46	47	48	49	50
Room	.000%	.000%	.000%	.000%	.000%
100	.013	.020	.005	.014	.013
150	.070	.060	.040	.046	.063
200	.100	.101	.084	.073	.108
250	.144	.139	.100	.101	.138
300	.133	.140	.112	.109	.170
350	.153	.157	.126	.141	.100
400	.173	.161	.136	.157	.106
450	.191	.157	.147	.179	.106
500	.217	.182	.175	.221	.058
550	.230	.203	.215	.273	-.083
600	.201	.226	.252	.328	-.509
650	.173	.242	.281	.362	-1.105
700	.135	.245	.314	.433	-1.433
750	.115	.240	.336	.487	-1.491
800	.108	.239	.354	.536	-1.515
850	.109	.254	.388	.570	-1.524
900	.120	.282	.448	.595	-1.526
950	.170	.332	.500	.597	-1.525
1000	.211	.415	.581	.593	-1.524
1050	.329	.520	.661.	.594	-1.523
1100	.480	.690	.810	.627	-1.530
1150	.523	.739	.835	.629	-1.526
1200	.546	.771	.841	.628	-1.518
1250	.560	.789	.840	.617	-1.517
1300	.576-	.805-	.800-	.600-	-1.514-
1350	.588	.806	.730	.538	-1.538
1400	.601	.764	.620	.451	-1.580
1450	.624	.720	.416	.401	-1.635
1500	.633	.615	.350	.334	-1.741

CURVE NO. 11

THERMAL EXPANSION OF PLASTER

SAMPLE NO. 9 - $\frac{W}{V} = 4.9$

SAMPLE NO. 12 - $\frac{W}{V} = 9.7$

CURVE NO. 12

~ THERMAL EXPANSION OF PLASTER (80%), SILICA (20%) ~

— SAMPLE NO. 10, $\frac{W}{S} = .47$

- - - SAMPLE NO. 11, $\frac{W}{S} = .36$

CURVE NO. 13

~ THERMAL EXPANSION OF PLASTER (60%), SILICA (40%) ~

— SAMPLE NO. 9, $\gamma = .45$

— SAMPLE NO. 14, $\gamma = .55$

CURVE NO 14

- THERMAL EXPANSION OF PLASTER (40%), SILICA (60%) -

CURVE NO. 15

~ THERMAL EXPANSION OF PLASTER (30%), SILICA (70%) ~

— SAMPLE NO. 3, $\phi = .42$

--- SAMPLE NO. 4, $\phi = .35$

CURVE NO. 16

~ THERMAL EXPANSION OF PLASTER (20%), SILICA (80%) ~

CURVE NO. 17

~ THERMAL EXPANSION OF PLASTER (10%), SILICA (90%) ~

— SAMPLE NO. 7, $\bar{x} = .34$ --- SAMPLE NO. 13, $\bar{x} = .33$

PERCENT EXPANSION

11
10
9
8
7
6
5
4
3
2
1
0

0 200 400 600 800 1000 1200 1400 1600 °F.

0 100 200 300 400 500 600 700 800 °C.

TEMPERATURE

CURVE NO. 18

~ THERMAL EXPANSION OF SILICA ~

— SAMPLE NO. 21 & 15

- - - SAMPLE NO. 23

- - - SAMPLE NO. 24

CURVE NO. 19

THERMAL EXPANSION OF PLASTER - SILICA MIXTURES (AT 1300°F)

— PURE MATERIALS (NO RETARDER ADDED)

-- SETTING TIME - 15 MINUTES

CURVE NO. 20

- THERMAL EXPANSION OF PLASTER (30%), SILICA (50%), TiO_2 (10%) -

SAMPLE NO. 16 $\frac{W}{P}$ 30

PERCENT EXPANSION

7
6
5
4
3
2
1
0
-1
-2

0 200 400 600 800 1000 1200 1400 1600 °F
0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CURVE NO. 21

~ THERMAL EXPANSION OF PLASTER (30%), SILICA, SODIUM SILICATE ~

— SAMPLE NO. 17, SILICA (60%), SODIUM SILICATE (10%) $\frac{y}{x} = .42$

--- SAMPLE NO. 23, SILICA (50%), SODIUM SILICATE (20%) $\frac{y}{x} = .41$

PERCENT EXPANSION

0 200 400 600 800 1000 1200 1400 1600°F
0 100 200 300 400 500 600 700 800°C

TEMPERATURE

10

9

8

7

6

5

4

3

2

1

0

CURVE No. 22

~ THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), CaF_2 (10%). ~

SAMPLE No. 15 $\frac{1}{2}$ -34

CURVE NO. 23

THEATICAL EXPANSION OF PLASTER (50%), SILICA (50%), ZNO (10-7)

SAMPLE NO. 15 4-1-18

--- TIME-TEMPERATURE CURVE OF SAMPLE NO. 18 ---

CURVE NO. 24

~ THERMAL EXPANSION OF PLASTER (30%), SILICA (68%), BORIC ACID (2%) ~

SAMPLE NO. 20, $\frac{w}{k} = .35$

CURVE NO 25

~ THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), Cr_2O_3 (10%) ~

SAMPLE NO. 25 $\frac{W}{P} = .35$

CURVE NO. 26

~ THERMAL EXPANSION OF CHROMIC OXIDE ~

SAMPLE NO. 26 4-51

PERCENT EXPANSION

10
9
8
7
6
5
4
3
2
1
0

0 200 400 600 800 1000 1200 1400 1600°F
0 100 200 300 400 500 600 700 800°C

TEMPERATURE

CURVE NO. 27

THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), CRISTOBALITE (10%)

— SAMPLE NO. 27 $\frac{W}{L} = .35$

-- SAMPLE NO. 24 $\frac{W}{L} = .35$

CURVE NO. 27

~ THERMAL EXPANSION OF PLASTER (30%), SILICA, Li_2CO_3 ~

— SAMPLE NO. 20, SILICA (67%), Li_2CO_3 (3%) $\alpha = .36$
 --- " " 32, " (63%) " (1%) $\alpha = .38$
 --- " " 31, " (65%) " (5%) $\alpha = .34$

PERCENT EXPANSION

1.1

1.0

.9

.8

.7

.6

.5

.4

.3

.2

.1

0

0 200 400 600 800 1000 1200 1400 1600 °F

0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CURVE NO. 29

~ THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), BERYL (10%) ~

— SAMPLE NO. 30 $\alpha = .35$

CURVE NO. 30

~ THERMAL EXPANSION OF PLASTER (30%), SILICA (50%), CaSiO_3 (10%) ~

SAMPLE NO. 34 $\frac{1}{2}$ - 40

PERCENT EXPANSION

10

8

6

4

2

0

-2

-4

-6

-8

-10

0

200

400

600

800

1000

1200

1400

1600°F

0

100

200

300

400

500

600

700

800°C

TEMPERATURE

CURVE NO. 31

- THERMAL EXPANSION OF PLASTER (30%), SILICA, VERMICULITE -

SAMPLE NO. 35 — SILICA (69.6%), VERMICULITE (.35%) $\frac{V}{P} = .35$

" " 36 — " (69.4%), " (1.50%) " = .35

" " 45 — " (60.0%), " (10.00%) " = .35

PERCENT EXPANSION

TEMPERATURE

CURVE NO. 32

~ THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), Al_2O_3 (10%) ~

SAMPLE NO. 37 $\alpha = .33$

PERCENT EXPANSION

10
9
8
7
6
5
4
3
2
1
0

0 200 400 600 800 1000 1200 1400 1600 °F
0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CURVE NO. 33

~ THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), CHROMITE (10%) ~

SAMPLE NO 38 $\frac{W}{P} = .33$

PERCENT EXPANSION

9
8
7
6
5
4
3
2
1
0

0 200 400 600 800 1000 1200 1400 1600 °F
0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CURVE NO. 34

- THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), BASOL (10%) -

SAMPLE NO 39 $\gamma = .33$

PERCENT EXPANSION

CURVE NO. 35

THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), FELDSPAR (10%)

SAMPLE NO. 40 $\frac{w}{p} = .35$

PERCENT EXPANSION

TEMPERATURE

CURVE NO. 36

THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), METRONITE (10%)

SAMPLE NO. 41 $\frac{W}{P} = 35$

PERCENT EXPANSION

10
9
8
7
6
5
4
3
2
1
0

0 200 400 600 800 1000 1200 1400 1600 °F
0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CURVE NO. 37

~ THERMAL EXPANSION OF NATURAL ANHYDRITE ~

CURVE NO. 30

~ THERMAL EXPANSION OF CALCIUM SULFATES ~

- ANHYDRITE (NATURAL) CaSO_4 , SAMPLE NO. 43, $\frac{W}{V} = .24$
- PLASTER, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, SAMPLE NO. 12, $\frac{W}{V} = .37$
- - - GYPSUM, $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$, SAMPLE NO. 50, $\frac{W}{V} = .26$

CURVE NO. 39

THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), WOLLASTONITE (10%) ~

SAMPLE NO. 44 $\frac{W}{P} = .35$

PERCENT EXPANSION

10
9
8
7
6
5
4
3
2
1
0

0 200 400 600 800 1000 1200 1400 1600 °F.
0 100 200 300 400 500 600 700 800 °C

TEMPERATURE

CURVE NO. 46

~ THERMAL EXPANSION OF PLASTER (30%), SILICA (60%), MgO (10%) ~

SAMPLE NO. 46

CURVE NO. 41

~ THERMAL EXPANSION OF PLASTER (30%), SILICA, LITHIUM FLUORIDE ~

TIME IN MINUTES

CURVE NO. 42

SETTING TIME (VICAT) OF PLASTER - SILICA MIXTURES
(NO ACCELERATOR OR RETARDER ADDED)

CURVE NO 43

~ TENSILE STRENGTH OF SILICA PLASTER MIXTURES ~

--- PURE MATERIALS (NO RETARDER ADDED)

— SETTING TIME - 15 MINUTES

TENSILE STRENGTH IN LBS./SQ. IN.

TABLE NO. IIIPHYSICAL PROPERTIES OF SILICA PLASTER MIXTURES

Sample No.	Thermal Expansion * 25 1300°F. (Percent)	Setting Expansion (Percent) in 1 hr.	Setting Time (Min.)	Tensile Strength (Lbs. sq. in.) (7 days)
1	.453	.256	11.	165.
2	.796	.260	11.5	120.
3	.273	.242	11.	226.
4	.641	.307	15.	<u>186.</u>
5	.832	.373	15.	126.
6	.500	.286	15.	267.
7	1.058	.039	12.	40.
8	-.076	.246	10.	310.
9	-1.180	.276	9.5	562.
10	-.542	.327	10.	438.
11	-.321	.355	15.	580.
12	-.968	.352	15.	725.
13	1.073	.128	15.	64.
14	.136	.432	15.	419.
15	1.343	---	30.	---
16	.396	.447	15.	170.
17	.912	---	15.	---
18	.506	.473	15.	229.
19	.229	.173	15.	117.
20	.755	.391	15.	86.
21	1.342	---	15.	---
22	1.332	---	--	---
23	1.280	---	--	---
24	1.085	---	15.	---
25	.524	.622	15.	223.

PHYSICAL PROPERTIES OF SILICA PLASTER MIXTURES

Sample No.	Thermal Expansion at 1300°F. (Percent)	Setting Expansion (Percent)	Setting Time (Min.)	Tensile Strength (Lbs./sq. in.) (7 days)
26	.520	---	--	---
27	.693	.503	15.	183.
28	.936	---	15.	---
29	.818	.117	15.	184.
30	.524	.403	15.	228.
31	.892	.018	15.	30.?
32	.857	---	15.	---
33	.545	---	15.	170.
34	.608	.077	15.	145.
35	.601	---	15.	---
36	.615	---	15.	---
37	.536	.522	15.	228.
38	.573	.477	15.	232.
39	.636	.419	15.	228.
40	.496	.505	15.	
41	.588	---	15.	---
42	.955	----	--	---
43	.880	---	--	---
44	.581	.142	15.	202.
45	.580	---	15.	210.
46	.576	.205	15.	267.
47	.805	---	15.	183.
48	.800	---	15.	167.
49	.600	.422	15.	101.
50	-1.524	---	--	---

INTERPRETATION OF RESULTS

THERMAL EXPANSION DATA

I. SILICA-PLASTER SYSTEM

(1) PLASTER - The thermal expansion of plaster itself (Curve No. 11) increases from room temperature to about 225 to 250°F (107 to 121°C) (the points cannot be seen directly from the curve since values were taken every 50°F). A contraction then begins with a more abrupt change at about 300°F (150°C), a slight increase follows and then an abrupt decrease in size follows from 500 to 700°F (260 to 371°C). There is very little change until 1000 to 1100°F (538 to 594°C). An expansion then takes place to 1400°F (760°C), a slight contraction to 1450°F (789°C), and then a very rapid contraction takes place amounting to as much as several percent in 100°F. These results correspond to those of Coleman (26), who used plaster where hydrocal was used in this research. The contraction is greater with a greater proportion of water to plaster in the original mix.

(2) SILICA - Curve No. 18 shows the thermal expansion of silica, Sample No. 21 being a very finely ground product and is used throughout the other tests. Samples NO's 23 and 24 consisted of coarser silicas. All samples have 3% plaster as a binder. The value for the thermal expansion of silica when in a finely divided aggregate and 3% plaster as a binder lies between those of Braesco (48) Curve No. 2.

An extrapolation of curve No. 19 of the silica-plaster system gives a value of 1.45% for the thermal expansion of 100% silica (quartz) at 1300°F. This value is only a few hundredths percent higher than that of Le Chatelier. This may be due to the difference in material or fineness. From curve No. 19 it would seem that the use of plaster as a binder gives results slightly lower than the values of the pure materials, especially when the material is not ground extremely fine, as is shown by the lower values of the expansion of silica when not so finely ground, samples 23 and 24, curve No. 19. The use of 3% plaster as a binder is recommended where convenience and comparative results only are desired.

The expansion curve of silica rises gradually and increases in rate several hundred degrees below the inversion point 1063°F. As shown by Braesco (48), Le Chatelier (11) and many others, there is no sharp increase at the inversion point of an aggregate like that occurring in a crystal, curve No. 1. This is probably due to the difference in structure of the specimen and flow of heat into the sample. Curve No. 18, sample No. 21, shows a rise in expansion to 1100 to 1150°F instead of 1063°F which is the inversion point. This is due to the use of the "mobile" rather than equilibrium method of heating.

(3.) THE SILICA-PLASTER SYSTEM

Curves No's 12 to 17 show the expansion of mixtures of plaster and silica. In these curves the contraction of plaster manifests itself while the high expansion of silica also manifests itself. The properties of each are manifested in proportion to the amount of each present.

Curve No.15 showing the expansion of a 30% plaster-70% silica mixture is used as an example since it is used as a basis of comparison in later curves and gives the greatest expansion of those mixtures with a fair tensile strength. The curve No.15 of sample No. 1 shows a break at 300°F, a contraction between 500 and 750°F, a slight standstill and then a rapid expansion to 1100°F, followed by a less rapid but regular expansion to 1500°F. With less water, sample No.4, the results are the same except that the contraction begins about 50° later and is smaller in amount. The final expansion is also higher. In the other samples the expansion up to 500°F is also different for varying ratios of $\frac{W}{P}$. This is no doubt due to the variance in amount of free water left in the sample and the rate of heating due to the difference in heat required to evaporate varying amounts of water. The fact that the curves of samples No. 1 and 4 are identical up to 500°F is no doubt a coincidence.

An explanation of this type of curve is given by Coleman (26) - "A shrink generally occurs at 255 to 300°F where there is a large proportion of plaster. An expansion follows to 480 to 660°F when a second shrinkage begins. In most cases this second shrinkage is much greater than the first and takes place over a much larger temperature range. It is probably due to the loss of the remaining water of crystallization. At about 750 to 840°F, a third expansion begins and continues to about 1100°F. After that the expansion is not very large in most investments." This author also shows that the difference in $\frac{W}{P}$ ratio affects the expansion very little.

The results coincide fairly well with the temperature limits as set by Coleman but do not agree with the latter's results regarding the $\frac{W}{P}$ ratio. It may be assumed, however, that the expansion of a given sample containing plaster will increase as the water is decreased, since the results of Coleman have been found to be the only exception known in the case of several hundred samples.

The interpretation of the results is on this basis as well as on the results found on sample No. 19, Curve No. 23 on which a time-temperature curve was run. This sample, although containing 10% of zinc oxide may be used instead of a pure silica-plaster mix since the zinc oxide showed no reaction which would interfere with the time-temperature curve.

At 220 to 250°F a slight decrease in the rate of expansion occurred, the expansion of the sample remained at a standstill at 225°F for some time. These facts are illustrated by the slow rate of increase in temperature. This is due to the elimination of free water and some combined water. The combined water continues to leave gradually with a slight slowing down at 320 to 350°F where all of the $1\frac{1}{2}\text{H}_2\text{O}$ of crystallization has probably left. There is a sharp contraction of the sample between 550 and 650°F, especially near 600°F, where the rate of rise of temperature is seen to decrease. Here the remaining $\frac{1}{2}\text{H}_2\text{O}$ of crystallization is leaving. The anhydrite has been formed entirely at 750°F.

The results may be likened to those occurring in the manufacture of plaster by the kettle process. When the material is heated to 225 to 250°F the free water and the $1\frac{1}{2}\text{H}_2\text{O}$ of crystallization leave, this formation of steam causes the mass to rise in the kettle, here plaster is formed (first settle stucco). The mass then becomes quiet and settles for some time. At a higher temperature the mass again begins to froth and rises much higher in the kettle than before, here the remaining $\frac{1}{2}\text{H}_2\text{O}$ of crystallization leaves; soon there is a quiet and the material formed, anhydrite, settles to a lower depth than before. This is true because of the greater density than before (page 26). The product is called "second settle stucco".

Based on the above analogy and curves 11 and 18, this is what probably happens in the heating of a plaster mixture containing silica (or other filler).

There is a fairly regular expansion of the material to 200 to 250°F, since the expansion of gypsum and silica are regular in this range. At 200 to 250°F the free water and part of the combined water leaves. This should cause a shrinkage of the material but the silica continues to expand and the continuous leaving of the water and bursting into steam does not permit the material to shrink. The rigidity and peculiar interlocking of the plaster and silica does not permit expansion due to the formation of steam since the material is somewhat porous. The continued expansion up to about 500°F is due in a large part to the expansion of the silica. From 500 to 750°F the remaining water of crystallization is leaving and permits the plaster volume to decrease sharply as is the case in the manufacture of "second settle stucco". The contraction is no longer prevented by a continuous formation of steam.

The explanation of the occurrences from 750 to 1500°F may be based on the following:

Curve No. 37 shows that anhydrite expands fairly regularly between 750°F and 1400-1450°F, after this a sharp contraction takes place. The expansion of silica from 750-1100°F is very great due to the inversion of alpha to beta forms. From 1100°F to 1500°F there is practically no change in size.

The silica-plaster curves show a sharp increase in expansion from 750 or 800 to 1100°F. The time temperature curve (No. 23) shows a decrease in rate of temperature rise at about 1050°F. This fact shows that the inversion of silica (alpha to beta) is an endothermic reaction on cooling the reverse is true (See Phenomina of Inversion, page 18). The temperature would probably have been closer to 1063°F if the time intervals were less than 5 minutes. After 1100°F the increase in expansion is due to that of anhydrite. The lack of a contraction as shown by plaster at 1400 to 1500°F is due to the refractoriness of the silica and structure of the aggregate, the construction takes place at a higher temperature in the presence of high melting refractory materials such as silica.

Curve No. 19 clearly shows the effect of $\frac{W}{P}$ ratio. The curves merge as the $\frac{W}{P}$ ratios approach each other showing that the retarder has little effect, if any.

II. OTHER MATERIALS

(1) Very Insoluble and of High Melting Point

The curves containing the following materials were found similar to those of plaster-silica mixtures:

1. Titanium Oxide
2. Calcium Fluoride
3. Zinc Oxide
4. Chromium Oxide
5. Cristobalite
6. Beryl
7. Calcium Silicate
8. Vermiculite
9. Aluminum Oxide
10. Chromite
11. Barium Sulfate
12. Feldspar
13. Metronite
14. Wellastonite
15. Magnesium Oxide

The differences in expansion of the samples containing the above mentioned were due to the differences in the expansion of the above ingredients.

For examples, cristobalite which has a greater expansion than silica, gave a greater expansion when substituted for a like amount of silica. This fact has been taken advantage of in commercial use where a mould with a high expansion is desired (65).

Chromite, Aluminum Oxide, and Beryl, Curves No's 33, 32 and 29 respectively, decreased the expansion of their respective samples in the order given, this was due to the lower expansion of the materials themselves as shown in Table II, Appendix.

(2) SLIGHTLY SOLUBLE SUBSTANCES - Sample No. 20 (Curve 24) shows that 2 percent of Boric Acid increases the thermal expansion considerably. There is but a small contraction from 350 to 500°F. Between 850 and 1000°F, there is a

decrease in rate of expansion. The latter is most probably due to the decomposition of Boric Acid into the anhydride, Boron Oxide. The lack of the shrinkage found in plaster and silica alone is most probably due to the fact that as shown in curve No. 7 the presence of materials which increase the vapor pressure of water will cause the formation of the anhydrite at lower temperature. The expansion of the anhydrite (curve No. 37) formed adds to that of the silica. The expansion of the boric acid itself may account for the increase in part but would hardly account for the elimination of the shrinkage near 600°F, unless the anhydrite is formed.

Samples 28, 31, and 32 show that Lithium Carbonate in amounts up to and possibly slightly above 3 percent increases the expansion of the material considerably. The addition of 5 percent Li_2CO_3 begins to decrease the expansion while amounts below 3 percent do not give as great a value. The shrinkage occurring after 1250° to 1300°F., is due to the decomposition of the carbonate or possibly to the part played by the Li_2CO_3 in decomposing the anhydrite. Again the formation of anhydrite at lower temperature is supposed. The fact that the increase of the salt (Li_2CO_3) above certain amounts begins to decrease the expansion shows that the expansion of the salt itself is not the entire cause of the increase in expansion. Similar to

the action of electrolytes in first accelerating and then retarding the setting of plaster when added in larger amounts, curve No. 10, so the action of salts begin to have an opposite action when added in too great a quantity.

Lithium Fluoride, Curve No. 41, gives results very similar to those of Lithium Carbonate but shows the effect of the addition of too much material to a much greater extent. The LiF is most probably decomposed into hydrofluoric acid and lithium oxide, as a nodule of glass was found on the sample and a hole was found above it in the movable quartz rod.

SETTING EXPANSION - The setting expansion of investments when mixed with enough water to give a "slump" consistency is not very definite, that is, the material does not give a definite setting expansion on consecutive readings. Thicker mixes have been found to give more consistent results.

The explanation given by Coleman (26) may be cited - "It will be noted that most of the materials tested expanded on setting, the amounts of expansion ranging up to .5 percent. In general the expansion increases as the plaster content increases, though this is not always true. Increasing the proportion of water decreases the expansion in most cases. It will be noted that investment No. 11

contracted 1.85% on setting. This may be due in part to the high water ratio necessary because of the extreme fineness of the powder and in part to the low plaster content."

The reasons for the setting expansion are still not known with much assuredness. Wiss, Camp, and Lades (63), state - "The Phenomina of apparent expansion (setting) has never been satisfactorily explained, although careful measurements have been made of it." The theories proposed by Davis, (25), page 31, as a change from rhombic to monoclinic gypsum is the best so far proposed. Even this can hardly explain the following phenomina: Dr. Scheu (61) showed that plaster investments expand up to 2.2% on setting if placed under water just after the initial set has taken place. Wilson (62) showed that certain plasters expand up to 4.4% by taking up moisture from the air. The moisture is utilized in supplying water of crystallization needed to complete the reaction taking place.

Other variables affecting the amount of setting expansion are temperature of water used and amount of spatulation.

In general, soluble substances decrease the setting expansion as shown in samples 29, 31 and 34.

SETTING TIME - The setting time was found to have been slightly increased as the amount of silica is increased. This is shown in curve No. 2. This is probably due to the

increase in ratio of the water to actual plaster present, also there is possibility of the formation of a slight amount of silicic acid on the surface of the silica. The rapid rise in setting time when the plaster is reduced below 10% is due to insufficient strength of the setting mix to support the Vicat plunger.

All other mixes were adjusted to 15 setting time, and Vicat tests were not performed on the virgin materials. The only appreciable accelerator was LiF, Sodium Silicate and Boric Acid were very mild retarders.

TENSILE STRENGTH - Curve No. 43 shows the tensile strength of the two series of silica plaster mixtures. As is the case with thermal expansion, the series with the lesser amount of water gives the higher values. As the $\frac{W}{P}$ ratio of the samples in the two series approach each other, the curves come closer together until they finally coincide. The curves showing tensile strength are practically straight lines, showing only a slight curvature in the high silica content mixtures.

The following materials were found to increase the tensile strength slightly - Calcium Fluoride, Chromic Oxide, Aluminum Oxide, Chromite, Barium Sulfate, and Magnesium oxide. The latter increased the tensile strength appreciably.

The following were found to decrease the tensile strength - Zinc Oxide, Boric Acid, Lithium Carbonate, and Calcium Silicate. The Zinc Oxide increased the $\frac{W}{P}$ ratio greatly which was the cause for its weakening action. Boric Acid and Lithium Carbonate are slightly soluble and probably interfere with crystallization or cause large sized gypsum crystals as shown by Weiser & Moreland (23) and explained on page 39. The calcium silicate formed a powdered surface and therefore formed a material with improper crystallization and binding properties.

MISCELLANEOUS Lithium carbonate when added in increasing amounts reduced the $\frac{W}{P}$ ratio, that is, it decreased the amount of water necessary to give the standard slump consistency. Lithium fluoride did likewise but was not so noticeable since ordinary plaster was used in this sample instead of the usual hydrocal, or alpha-gypsum.

CHAPTER VII

SUMMARY

SUMMARY

THE SYSTEM SILICA-PLASTER, AND MODIFIERS

Mixtures of silica and plaster were made with varying proportions of water and the following properties were studied on these mixtures adjusted to equal consistency:

1. Thermal Expansion
2. Setting Expansion
3. Setting Time
4. Tensile Strength

Table III shows the results of all of the tests. More detailed results on the thermal expansion are given in curves 11 to 41 and in Table II.

In the system Silica-Plaster, an increase in the percentage of silica increases the thermal expansion, the setting expansion varies irregularly, the setting time is increased and the tensile strength decreases regularly.

An increase in the proportions of water to powder decreases the thermal and setting expansions, tensile strength, and increases the setting time.

The substitution of inert materials or modifiers for part of the silica raises the thermal expansion of the sample if the expansion of the substance is greater than that of silica and lowers it in direct proportion as its expansion is lower than that of the silica it displaced.

The effect of inert materials on the other properties is about the same as that of silica.

The substitution of inorganic materials which are somewhat soluble in water for part of the silica increase the thermal expansion, decreases the setting expansion and tensile strength, and in general decreases the setting time.

The effects of other materials on the above properties of silica-plaster mixtures are being studied further and will be published at a later date.

CHAPTER VIII

BIBLIOGRAPHY

Bibliography

- (1.) BOYLE, R., An Essay About the Originæ and Virtues of Gems, London, 1672.
- (2.) BERGMANN, T., De Terra Gemmarum, Upsala, 1777.
- (3.) LAVOISIER, A. L., Traite Elementaire de Chimie, Paris, 1789.
- (4.) DAVY, H., Phil., Trans., 100, 16, 1810.
- (5.) DES CLOISEAUX, Memoire Sur La Cristallization et La Structure Interieure du Quartz, Ann. Chim. et Phys. (3), 45, 129-316, 1855.
- (6.) ROSE, G., Uber Das Krystallisationssystem des Quarzes, Phys. Abhandl. Akad. Wiss., Berlin, 217-274, 1844.
- (7.) FIZEAU, H., Rechercher Sur La Dilatation et La Double Refraction du Cristal de Roche Echauffee, Ann. Chim. et Physique 2, 143-185, 1864; Ann. Physik u. Chem. (Poggendorff) 123, 515-526, 1864.
- (8.) MACE DE LEPINAY, J., BUISSON, H., and BENOIT, J. R., Determination du Volume du Kilogramme d'Eau, Trav. Mem. Bur. Int. Poids et Mesures, 14, 277 p.p., 1910.
- (9.) VOM RATH, G., Verlaufige Mittheilung uber eine neue Krystallform der Kieselsaure, Ann. Phys. u. Chem. (Poggendorff), 133: 507-508, 1868. Monatsb. K. Pr. Akad. Wiss. Berlin, 201-206, 1868.

Bibliography (cont'd.)

- (10.) VOM RATH, G., Ueber Cristobalit vom Cerro S. Cristobal bei Pachuca (Mexico), Neues Jahrb. Min. etc., I: 198-199, 1887.
- (11.) LE CHATELIER, H., Sur la dilatation du quartz, Compt. rend. Acad. Paris 108, 1046-1049, 1889.
- (12.) MALLARD, E., Sur la tridymite et la christobalite, Bull. Soc. Franc. Mineral. 13: 161-179, 1890. Compt. rend. Acad. Paris 110: 964-967, 1890.
- (13.) FENNER, C. N., The stability relations of the silica minerals, Amer. Journ. Sci. 36: 331-384, 1913. Zeitschr. anorg. Chem., 85: 133-197, 1914. Preliminary publication in Journ. Wash. Acad. Sci. 2, 471-480, 1912.
- (14.) BRAGG, W. H., The X-ray Spectra Given by Crystals of Sulphur and Quartz, Proc. Roy. Soc. London 89: 575-580, 1914.
- (15.) KYROPOULOS, S., Zur Unterscheidung der Aggregatzustände Verschiedener SiO_2 Arten Mittels Ihrer Röntgenstrahlen-Interferenzbilder, Zeitschr. anorg. allg. Chem. 99: 197-200, 1917.
- (16.) GIBBS, R. E., The variation with Temperature of the Intensity of Reflection of X-rays from Quartz and its Bearing on the Crystal Structure, Proc. Roy. Soc. London A 107: 561-570, 1925.

Bibliography (cont'd.)

- (17.) MAUGUIN, C., Utilisation possible des diagrammes de diffraction des rayons X pour la détermination complète de la structure de quartz, Compt. rend. Acad. Paris 173: 719-721, 1921.
- (18.) WYKOFF, R. W. G., Structure of Crystals, A. C. S. Monograph No. 19, Chem. Cat. Co., 1924.
- (19.) MACQUER, P. J., Mem. Acad., 678, 1747.
- (20.) MARGROFF, A. S., Mem. Acad. Berlin, 144, 1750.
- (21.) LAVOISIER, A. L., Mem. Acad., 341, 1768.
- (22.) LE CHATELIER, H., Recherches Experimentales Sur La Constitution Des Mortieres Hydrauliques, Paris, 1887.
- (23.) WEISER, H. B., and MORELAND, F.E., The setting of Plaster of Paris, Jour. Phys. Chem. 36, 1-30, 1932.
- (24.) VAN'T HOFF, Z. Physik. Chem. 45, 257, 1903.
- (25.) DAVIS, W. A., Journ. Soc. Chem. Industry, 26, 727, 1907.
- (26.) COLEMAN, R. L., Physical Properties of Dental Materials, Bureau of Standards Journal of Research, Dec. 1928. (Research Paper No. 32.)
- (27.) TAYLOR, N. O., PAFFENBARGER, G. C., and SWENNEY, W. T., Dental Inlay Casting Investments: Physical Properties and a Specimen, Jour. A. D. A., Dec. 1930.

Bibliography (Cont'd.)

- (28.) SOSMAN, R. B., The Properties of Silica, (page 413)
A. C. S. Monograph No. 37, Chem.
Catalog Co., 1927.
- (29.) SOSMAN, R. B., See No. 28, pp. 413-414.
- (30.) SOSMAN, R. B., See No. 28, Chap. XV.
- (31.) BATES & PHELPS, See No. 28, pp. 122.
- (32.) DAILEY, M. E., Private Communication, 1935.
- (33.) KOZU, S., and SAIKI, S., Sci. Rep. Tohoku Imp. Univ.
Third Ser. 2, 203-228, 1925. Also Jap.
Jour. Astron. Geophys. 2, 107-114, 1924.
- (34.) VAN'T HOFF, J. H., and ARMSTRONG, E. F., Sitzber Akad.
Berlin 563, 1900.
- (35.) GLASENAPP, M., Tonind, Ztg. 32, 1148, 1197, 1230, (1908).
- (36.) KEANE, A. L. Journ. Phys. Chem. 20, 701, 1916.
- (37.) FRISWELL, R. J., Journ. Soc. Chem. Ind. 26, 737, 1907.
- (38.) GRIMSLEY, G. P., The gypsum of Michigan and the Plaster Industry, Lansing 1904.
- (39.) MICHAELIS, W., Chem. Ztg., 17, 982, 1893.
- (40.) KEISERMANN, Kolloidchem. Beihefte, 1, 423, 1910.
- (41.) von WEIMARN, Zur Lehre Von den Zustanden der Materie,
1914.
- (42.) MARIGNAC, Ann. Chim. Phys., (5) 1, 274, 1874.
- (43.) RANDEL, W. S., and DAILEY, M. C., U.S. Patent No.
1,901,051.
- (44.) FIZRAU, H., Comp. Rend. 66, 1005, 1072, 1868.

Bibliography (cont'd)

- (45.) SOUDER, W., and HIDNERT, P., Measurements on the Thermal Expansion of Fused Silica, Scientific Paper of the Bureau of Standards, No. 524, 1926.
- (46.) MERRITT, G. E., The Interference Method of Measuring Thermal Expansion, Bureau of Standards Research Paper No. 515, 1933.
- (47.) SOUDER, W., HIDNERT, P., and FOX, J. F., Autographic Thermal Expansion Apparatus. Bureau of Standards Research Paper No. 722, 1934.
- (48.) BRAESCO., P. Etude des Points de Transformation Par Une Methode Dilatometrique, Ann. Physique, 14, 5-75, 1920.
- (49.) SWEENEY, W. T., Cristobalite For Dental Investment. Jour. A.D.A. Jan. 1933.
- (50.) PFAFF, F., Pogg. Ann. 107, 148, 1859.
- (51.) Smithsonian Tables, Smithsonian Institute, Wash.
- (52.) International Critical Tables, McGraw-Hill Co.
- (53.) GELLER, R. F., and INSLEY, H., Thermal Expansion of Some Silicates of Elements in Group II of The Periodic System. Bureau of Standards Research Paper No. 456.
- (54.) HEINDL, R. A., The Thermal Expansion of Refractories to 1800°C. Bureau of Standards Research Paper No. 562.
- (55.) HODSMAN, H. J., and COBB, J. W., Jour. Soc. Glass Tech.

Bibliography (Cont'd)

- 3, 201, 1919; Jour. Soc. Chem. Ind. 34, 465, 1915.
- (56.) SOUDER, W. H., and HIDNERT, P., Bureau of Standards Scientific Paper No. 352, 1919-1920.
- (57.) KOPP, H., Liebig's Ann. Suppl. 3, 289, 1865.
- (58.) DEVELLE, H. St. CL., and TROOST, L., Comp. Rend. 59, 162, 1864.
- (59.) VAIL, J. G., Soluble Silicates in Industry. A.C.S. Monograph No. 46. Chem. Cat. Co. 1928.
- (60.) WINKLEMAN, A. and SCHOTT, O., Wied. Ann., 51, 736, 1894.
- (61.) SCHEU, C. H., A new Precision Casting Technic, Jour. A.D.A., April 1932.
- (62.) WILSON, GEO. H., Manual of Dental Prosthetics, Lea and Febiger Co., Phila., 1917.
- (63.) WISS, J. E., CAMP, T. P., and LADOO, R. B., Gypsum Plasters in the Ceramic Industries, Jour. Amer. Ceram. Soc., May 1930.
- (64.) TAYLOR, N. O., PAFFENBARGER, G. C., and SWEENEY, W. T., Dental Inlay Casting Investments: Physical Properties and a Specification, Jour. A.D.A., Dec. 1930.
- (65.) COLEMAN, R. L., and WEINSTEIN, L. J., U. S. Patent No. 1,932,202, 1933.

CHAPTER IX

APPENDIX

APPENDIXTABLE IThermal Expansion of Minerals (50)

Mineral		Coeff. (linear, per °C) 0 - 100°C $\times 10^{-6}$	Coeff. (cubi) $\times 10^{-6}$	Coeff. L (avg.) * $\times 10^{-6}$
<u>Regular System</u>				
Garnet		8.478	25.434	
Fluorspar		19.504	58.512	
Magnetite		9.540	28.620	
Pyrites		10.084	30.252	
Galena		18.594	55.782	
<u>Tetragonal</u>				
Cassiterite	a	4.526	13.89	4.63
	c	4.860		
Vesuvianite	a	9.628	27.00	
	c	7.872		9.00
Zircon	a	11.054		
	c	6.264	28.35	9.45
<u>Hexagonal</u>				
Beryl	a	0.131	01.05	.35
	c	1.721		
Corundum	a	6.551	19.95	6.65
	c	6.875		
Tourmaline	a	7.732	21.81	7.27
	c	9.369		
Quartz	a	15.147	38.40	12.80
	c	8.073		
Calcite	a	3.105	20.10	6.70
	c	26.261		
Siderite	a	5.388	26.88	8.82
	c	16.133		
Apatite	a	10.006	31.23	10.41
	c	11.254		

* = Coeff. (cubical) divided by 3.

Rhombic

Mineral		Coeff. (linear)	Coeff. (cubi)	Coeff. L (Avg.)
Topaz	a	8.325	21.37	7.12
	b	8.362		
	c	4.723		
Aragonite	a	10.781	58.02	19.34
	b	15.903		
	c	315.58		
Borite	a	14.311	51.90	17.30
	b	22.519		
	c	14.904		
Celestite	a	19.205	52.61	17.54
	b	18.513		
	c	14.903		

Monoclinic

Adularin	a	15.617	17.94	5.98
	b	0.659		
	c	2.914		
Hornblende	a	8.119	28.45	9.48
	b	0.843		
	c	0.9530		
Diopside	a	8.125	23.30	7.77
	b	16.963		
	c	17.07		
Gypsum	a	15.519	75.00	25.00
	b	36.278		
	c	22.752		

APPENDIXTABLE IILinear Coefficient of Expansion of Materials

Material	Temp.	Coeff. (linear) $\times 10^{-6}$	Reference
Adularia	0-100	5.98	50
Adularia		2.030	44
Aluminum	40	23.13	51
Aluminum	600	31.50	51
Aluminum Oxide	25-900	7.2 to 8.0	52
Anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)	20-300	4.3	53
Antimony	40	11.52	51
Apatite	0-100	10.41	50
Aragonite	0-100	19.34	50
Arsenic	40	05.59	51
Augite		8.657	44
Barite	0-100	17.30	50
Bauxite Calcined (Heated to 1400)	20-1100	6.7	54
Beryl ($3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$)	20-300	Avg. 1.6	53
Beryl	0-100	.35	50
Bismuth	40	13.46	51
Brass, Cast	0-100	18.75	51
Cadmium	40	30.69	51
Calcite	0-100	6.70	50
Calcium Metasilicate ($\text{CaO} \cdot \text{SiO}_2$)(alpha)	20-200	11.7	53

Material	Temp.	Coeff. (linear) $\times 10^{-6}$	Reference
Cassiterite	0-100	4.63	50
Carbon (graphite)	40	7.86	51
Celestite	0-100	17.54	50
Celsian ($\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$)	20-400	3.4	53
China Clay	195	5.71	55
China Clay	450	4.95	55
China Clay	700	4.77	55
China Clay	900	4.69	55
Chrome Ore (Cuban) (Heated to 1400°C)	20-700	7.6	54
Chrome Ore (Cuban)	700-1000	20.5	54
Chrome Ore (Cuban)	1000-1200	8.9	54
Chrome Ore	25-1000	9.0	52
Cobalt	40	12.36	51
Copper	40	16.78	51
Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$)	25-400	1.3	53
Corundum (Al_2O_3)	20-600	7.9	53
Corundum	0-100	6.65	50
Corundum (Artificial) (Heated to 1425)	20-1485	7.8	54
Diaspore (Heated to 1400)	20-1275	7.5	54
Dicalcium Aluminum Silicate ($2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$)	20-400	8.1	53
Diopside	0-100	7.77	50
Epidote	40	7.778	44
Fire Brick (80% Alumina) (Heated to 1485)	20-1570	6.8	54

Material	Temp.	Coeff. (linear) $\times 10^{-6}$	Reference
Fireclay Brick (Q)	20-1120	5.8	54
Fluorspar	0-100	19.50	50
Forsterite ($2\text{MgO} \cdot \text{SiO}_2$)	20-304	8.3	53
Galena	0-100	18.59	50
Garnet	0-100	8.37	50
Glass, thermometer normal	0-100	8.1	51
Gold	40	14.43	51
Gypsum	0-100	25.00	50
Hornblende	0-100	9.48	50
Ice	-20 to -1	51.0	51
Iceland Spar parallel to axis	0-80	26.31	51
Iceland Spar perpendicular to axis	0-80	5.44	51
Indium	40	41.70	51
Iron (steel)	40	13.22	51
Kentucky Ball Clay No. 4 (Heated to 1400)	20-200	10.8	54
Kentucky Ball Clay No. 4	200-1400	5.2	54
Kentucky Ball Clay No. 4	1400-1490	47.2	54
Lead	40	29.94	51
Limestone (Indiana)	25-100	9.	56
Limestone (Indiana)	100-200	17.	56
Limestone (Indiana)	200-300	22.	56

Material	Temp.	Coeff. (linear) X10 ⁻⁶	Reference
Magnesite (Elec.Fused) (Heated to 1580°C)	20-1355	14.0	54
Magnesium	40	26.94	51
Magnetite	0-100	9.54	50
Marble	15-100	11.7	51
Mullite (3Al ₂ O ₃ ·2SiO ₂)	20-1100	5.3	53
Mullite (Synthetic)(Ht.)	20-1430	5.5	54
Nickel	40	12.79	51
Orthoclase	15-99	5.67	57
Periclase Brick (California) (Heated to 1000)	20-1420	13.6	54
Phosphorus	40	125.30	51
Platinum	40	8.99	51
Porcelain	20-790	4.13	51
Porcelain	0-1500	5.3	58
Potassium	0 to 50	83.00	51
Potassium Chloride	0-100	36.5	51
Potassium Nitrate	0-100	65.6	51
Potassium Sulfate	20	35.85	51
Pyrites	0-100	10.08	50
Quartz	0-100	12.80	50
Quartz	0-573	18.9	48
Quartz (Parallel)	0-80	7.97	51
Quartz(perpendicular)	0-80	13.37	51
Quartz (fused)	16-1000	.58	51

Material	Temp.	Coeff. (linear) $\times 10^{-6}$	Reference
Rock Salt (NaCl)	40	12.80	51
Rock Salt (NaCl)	50-60	18.9	51
Selenium	40	7.97	51
Siderite	0-100	13.37	50
Silica Brick	20-300	.58	54
Silica Brick	300-1135	40.00	54
Silica Brick	1135-1665	40.40	54
Silicon	40	36.80	51
Silicon Carbide (Heated to 1400)	20-1525	4.9	54
Silver	40	19.21	51
Sodium	20	71.0	51
Sodium Silicate 1:2 ratio		13.46	59
Spinel(Mg).Al ₂ O ₃)	20-1410	8.5	53
Sulfur	40	64.13	51
Thallium	40	30.21	51
Topaz	0-100	7.12	50
Tourmaline	0-100	7.27	50
Topaz	40	7.12	44
Vesuvianite	0-100	9.00	50
Wollastonite		28.00	60
Zinc	40	29.18	51
Zinc Aluminate (ZnO.Al ₂ O ₃)	20-525	7.7	53
Zircon	0-100	9.45	50

Material	Temp.	Coeff. (linear) $\times 10^{-6}$	Reference
Zircon Brick (A) (Heated to 1700)	20-1370	4.8	'54
Zinc Orthosilicate ($2\text{ZnO} \cdot \text{SiO}_2$)	20-350	1.6	54