

A TRIBUTE TO
**“Expansion of Concrete
through Reaction between
Cement and Aggregate”**

by Thomas E. Stanton

Foreword by Michael D.A. Thomas



Thomas Elwood Stanton Jr. was born in Los Angeles in 1881. He graduated from Saint Vincent's College in 1899 and received a BSc in mining engineering from the University of California, Berkeley, CA, in 1904. After working for the City of Los Angeles, he joined the California Division of Highways in 1912 where he enjoyed a distinguished career until he retired in 1951. He was awarded ACI's Wason Medal for Materials Research in 1939 and ASCE's Norman Medal in 1943. In addition to his outstanding contributions to the understanding of concrete materials, of which the following paper is one of many, he organized the California State Employees' Association and the State Employees' Retirement System.

In December 1940, the American Society of Civil Engineers (ASCE) published a paper by Thomas Stanton that most would consider to be the first definitive work on what was then termed cement-aggregate reaction, but has since become known as alkali-aggregate (or alkali-silica) reaction. In fact, Stanton published an earlier paper¹ in the Engineering News Record in February of the same year reporting preliminary findings from his studies, which identified the alkalis as the constituent of the cement involved in the reaction and first proposed that a limit be placed on the cement alkalis (0.50% Na₂O_{eq}) for certain localities. Stanton's paper in the ASCE Proceedings, however, presented full details of these studies,

¹ Stanton, T.E., 1940, Engineering News Record, February 1, pp. 59-61.

10 Stanton

which were initiated in response to the “failure” of a concrete pavement in 1938, just 1 or 2 years after construction. Other structures in Monterey County had shown similar types of distress in the form of map cracking (see Fig. 1 in Stanton’s paper), one of which, the King City Bridge, particularly intrigued Stanton because it was the first case that really attracted the attention of a number of agencies whose investigations produced an equal number of speculative causes, which Stanton suggests were “in the category of interesting theories” leaving “an unsolved mystery.”

The discoveries reported in Stanton’s paper were not limited to the occurrence of a reaction between constituents of the cement and the aggregate, but included many phenomena that have since been “rediscovered” by numerous investigators many times over; the contributions Stanton made in this paper include the following:

- A test method, involving measuring the expansion of mortar bars stored over water in sealed containers, was developed to determine whether specific cement-aggregate combinations would produce deleterious expansion; Stanton modestly confessed this to be an accidental discovery. The test method formed the basis for the ASTM C227 Mortar-Bar Test, which still survives “on the books” at ASTM, although it is now well-established that the test fails to identify many slowly-reacting aggregate types. In a later paper published in 1943,² Stanton reported that the expansion could be accelerated by storing the mortar bars at higher temperatures (110 °F) or by immersing them in solutions of sodium hydroxide (at 70 or 110 °F). The latter approach is, of course, the precursor to the accelerated mortar bar test, which was rediscovered without reference to Stanton’s work almost 50 years later. It is interesting to note that while Stanton says the approach has “definite possibilities,” he also cautions against adopting these tests without first establishing a correlation with field experience, a step that often seems to be missing with some of the test procedures and associated test limits being proposed today!
- It was observed that only certain types of aggregate caused expansion, indicating the importance of aggregate mineralogy. However, such aggregates did not always cause expansion, implying that other conditions had to be met.
- The “other condition” was that alkalis from portland cement had to be present in sufficient quantity. Stanton concluded that the expansion was negligible when the cement alkalis were below 0.60% Na₂O. This formed the basis for the definition of low-alkali cement and the limit is still referred to in many specifications today, being an optional requirement in ASTM C150 for portland cement and a suggested measure for preventing expansion with reactive aggregates in the appendix of ASTM C33 for concrete aggregates. However, since this time, many researchers have shown that deleterious expansion can occur with low-alkali cement and that it is the total alkali content in the concrete that needs to be considered when controlling damaging reaction.
- Stanton reported that a chemical reaction between the alkali hydroxides and certain forms of hydrous silica, such as opaline silica, in the aggregate

² Stanton, T.E., 1943, *ASTM Proceedings*, Vol. 43, pp. 875-893.

produced an alkali-silica gel, which was often found at the base of popouts and exuding from cracks. Although he didn't provide a mechanism for the resulting expansion and cracking of concrete, he implied that this reaction may be the root cause.

- The greatest expansion in Stanton's tests were observed with a siliceous magnesian limestone. In an effort to explain this, Stanton conjectured that the reaction between magnesium carbonate and alkali hydroxide, the occurrence of which he confirmed by experimentation, may lead to expansion. Although, he didn't coin the term "dedolimitization," this is the first reference in the literature to an "alkali-carbonate reaction." Chemical equations and calculations of volume increase due to the formation of a hydrated sodium carbonate are given in the paper. Later Stanton reported³ that it was opaline silica in the chert that was the cause of deleterious reaction with this rock.
- Early tests showed that a pozzolanic cement exhibited less expansion when combined with a reactive aggregate than might be predicted based on the alkali content of the cement. In follow-up tests, he demonstrated that 25% ground pumice (a pozzolan) eliminated deleterious expansion, whereas 25% ground quartz (Ottawa) sand did not, indicating that the beneficial action of the pozzolan extended beyond merely diluting the cement alkalis.
- Expansion tests with the siliceous magnesian limestone showed that expansion occurred when the aggregate was present in the amount of 1% (by mass of aggregate), that expansion was a maximum when 20% of the aggregate was present, and that there was little or no expansion when the reactive aggregate comprised 40% or more of the total aggregate. Although, Stanton did not coin the term himself, this phenomenon has become known as the "pessimism effect."
- Another serendipitous discovery was the role of the particle size of the reactive aggregate. Stanton theorized that expansion would increase as the surface area of the reactive aggregate increased. This proved to be correct to some extent as he observed the expansion to increase and reach a maximum when the siliceous magnesian limestone (used at a level of 5% of the total mass of aggregate) was crushed to pass the #30 sieve while being retained on the #80 sieve. However, he also observed that expansion was eliminated when the reactive aggregate was ground to pass the #80 sieve, showing that finely ground reactive silica does not lead to deleterious reaction. He surmised that this was due to either the reaction being so finely dispersed throughout the system that it did not produce sufficient expansive stresses or the reaction being largely complete before the concrete reached permanent set.
- Stanton also recognized that expansion due to the reaction may not always lead to failure of the concrete, but that the resultant cracking could promote attack of the concrete or embedded steel reinforcement due to seawater or other deleterious solutions.

Thus, in addition to discovering alkali-aggregate reaction, Stanton provided insight as to the probable mechanism, developed a test for evaluating specific

³ Stanton, T.E., 1944, Discussion appearing in the ACI JOURNAL, *Proceedings* Vol. 40, pp. 573-580.

12 Stanton

material combinations, suggested possible cures by limiting the cement alkalis or using a pozzolan, and made some interesting observations on the phenomenology of the reaction.

The impact of Stanton's findings cannot be overstated. Prior to his publication, aggregates were considered to be inert filler, but after it was clear that some aggregates were not suitable for use in concrete without special measures. Of course, Stanton's findings that cement alkalis could influence the durability of concrete caused great concern for the cement companies which were just coming to terms with the role of C_3A in determining sulfate resistance. Perhaps the most disturbing implication of Stanton's study was that concrete could "fail ... even if it is exposed to only normal curing and weathering conditions."

Stanton's discoveries spawned a multitude of research and the two decades that followed saw the publication of a number of seminal papers that are still required reading for today's students of alkali-aggregate reaction. Research continues in this area and later this year will see the staging of the 13th International Conference on Alkali-Aggregate Reaction (ICAAR) in Trondheim, Norway. The significance of Stanton's paper can be measured by the number of papers that will undoubtedly begin with reference to his findings of almost 70 years before. Perhaps of more immediate importance is that Stanton's work provided answers to agencies puzzled by the occurrence of mapcracking in their structures (for example, the Parker Dam) and allowed them to take measures to avoid problems in the construction of new facilities in the years that followed, an example of this being the use of pozzolans in the construction of the Davis Dam.

In summary, Stanton's paper represents a landmark in concrete technology because it embodies many of the principals of engineering, these being the correct identification of a problem, the elucidation of its mechanisms and the development of practical solutions to prevent its reoccurrence – all in one paper! Read it and you will be inspired!

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P A P E R S

EXPANSION OF CONCRETE THROUGH
REACTION BETWEEN CEMENT
AND AGGREGATEBY THOMAS E. STANTON,¹ M. AM. SOC. C. E.

SYNOPSIS

Tests have demonstrated that excessive expansion of concrete may occur through chemical reactions between cements of relatively high alkali content and certain mineral constituents in some aggregates, such as certain types of shales, cherts, and impure limestones found along the coast of California between Monterey Bay on the north and Los Angeles County on the south. A new test procedure is described in this paper through which it is possible, in a comparatively short time, to develop the deleterious characteristics of cement-aggregate combinations similar to those reported in the California study. The procedure consists of curing the specimens in sealed containers at normal temperatures.

INTRODUCTION

Numerous tests conducted during recent years have established the value of low-heat cements in minimizing the shrinkage of concrete, and the value of the sulfate-resistant standard and puzzolanic-type cements in resisting attack by the sodium and magnesium sulfates and other deleterious constituents in alkali soils and sea water. Designers must now consider a third important factor in cement composition which may so affect the characteristics of a portland cement concrete as to produce excessive expansion and possible ultimate failure of a structure even if it is subjected to only normal curing and weathering conditions.

Given a properly designed cement-aggregate combination, such a condition can occur even when the cement is perfectly sound (in the generally accepted interpretation of the word) and of such a chemical composition as to be highly resistant to exterior attack by deleterious agents. This is fully and conclusively demonstrated through the tests described in this paper. A new test

NOTE.—Written comments are invited for immediate publication; to insure publication the last discussion should be submitted by April 15, 1941.

¹ Materials and Research Engr., State Div. of Highways, Sacramento, Calif.

procedure is also described without which it would probably have been impossible to make the laboratory tests.

Continual wetting or alternate wetting and drying of test specimens failed to develop (in any reasonable period of time, at least) any of the abnormal expansion characteristics experienced on many projects in certain districts of the state. It is now known that at least some of the field conditions of expansion can be duplicated in the laboratory when the specimens are cured in sealed containers, thereby retaining the original mixing water with few, if any, additions or subtractions through immersion or drying. It was not until this fact was discovered that invariable measurable expansion was obtained with certain cement-aggregate combinations, and that negligible, if any, expansion occurred with other combinations.

The complete documentary evidence sustaining the conclusions of the tests are presented for the first time in this paper, although a very brief preliminary report has been presented elsewhere.²

SALINAS VALLEY PAVEMENT FAILURE

Early in 1938, a section of concrete pavement north of the town of Bradley in the Salinas Valley, Monterey County, Calif., failed because of excessive expansion. An intensive field and laboratory investigation followed to determine the causes of the failure and to develop safeguards to prevent a recurrence of the condition in future work. The failed pavement was built in the fall, winter, and spring of 1936–1937. Most of it had passed through two winters when portions began to show distress in the spring of 1938. The distress became manifest in the form of excessive expansion which caused buckling at the expansion joints and a severe cracking throughout the length of certain slabs (Fig. 1(a)).

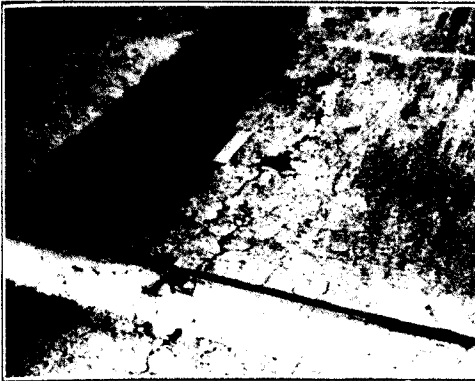
A coarse aggregate from a local commercial plant, located on a tributary to the Salinas River, was used throughout. The fine aggregate came from two sources, one the local deposit (herein referred to as Oro Fino), from which all of the coarse aggregate was secured, and the other (Coyote) imported from a commercially operated deposit near San Jose, Calif., in the San Francisco Bay area. The sands from these two deposits were used during alternate periods so that it was easy to identify the source of the fine aggregate in each section or day's run. A close inspection of all sections readily disclosed that excessive expansion had occurred only in those sections in which the local (Oro Fino) fine aggregate had been used, and it was obvious, therefore, that aggregates from this area contained at least one of the sources of trouble.

EARLIER FAILURES

The Bradley pavement failure culminated a series of concrete failures along the coast area from Monterey County in the north to the northern part of Los Angeles County in the south, throughout which aggregates of the same typical characteristics are encountered.

The first structure in which distress developed to such an extent as to attract attention was the King City Bridge (Fig. 1(e)) built in 1919–1920

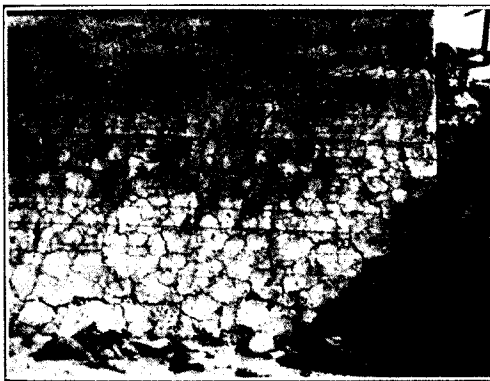
² "Influence of Cement and Aggregate on Concrete Expansion," by Thomas E. Stanton, *Engineering News-Record*, February 1, 1940, p. 59.



(a) Pavement



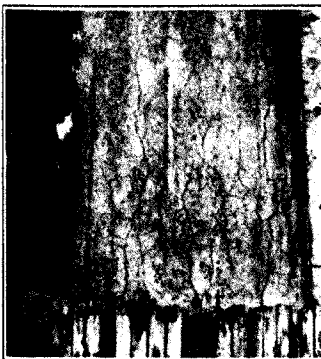
(b) Bridge Girder



(c) Sea Wall



(d) School Building



(e) Bridge Pier



(f) Bridge Pylon

FIG. 1.—TYPICAL CONCRETE FAILURES RESULTING FROM COMBINATIONS OF CERTAIN AGGREGATES AND HIGH-ALKALI CEMENTS

across the Salinas River at King City, Monterey County. This bridge consists of an all-concrete trestle approach to a series of concrete piers and steel trusses over the main channel of the river. The channel structure consists of steel trusses resting on concrete piers of two circular sections with battered sides connected by a 12-in. diaphragm wall.

The coarse aggregate was imported from an unquestioned source, but the fine aggregate was taken from the bed of the Salinas River, or a small tributary (Pine Creek) emptying into the river a short distance upstream from the bridge.

Within three years after construction, well-defined cracks were in evidence in the caps of the piers. Later, these cracks extended into the columns of the piers. By July, 1924, all of the pier caps were more or less affected.

The concrete in the pile and trestle construction has shown little, if any, distress, the severe distress being confined to the piers. Although it is possible that the cement was not of a uniform quality, so far as is known the two concretes differed only in the sands used. Pine Creek sand was used at first; then sand from pits in the stream bed of the Salinas River and later surface sand from the bed of the same river, deposited during the winter rains, was used.

The condition of the King City Bridge has been investigated by a number of agencies, including representatives of the Bureau of Public Roads, the Bureau of Standards, the Portland Cement Association, and the cement companies, as well as engineers and chemists of the California Division of Highways. In general, the number of opinions expressed equaled the number of reports made. The causes of failure advanced by the different investigators were the sand; unsound cement; excess water; extreme variations in temperature; faulty curing; faulty concrete design; variable coefficient of expansion between different parts (including reinforcing steel); electrolysis; overstressing or under design; and rusting of anchor bolts, reinforcing steel, iron pipes, washers, etc. All of the assumed causes, however, were purely speculative without any substantiating foundation and (in 1940) have remained in the category of interesting theories.

The King City Bridge has been emphasized because it was the first partial failure of a major structure to attract attention and because the definite cause of the difficulty has been an unsolved mystery. Subsequent to the King City Bridge trouble, several concrete trestles, built afterward in Monterey County, in which fine aggregate from the Salinas River or its tributaries had been used, developed serious distress (Fig. 1(b)).

Similar trouble had been noted in Ventura County where the concrete piers of the Southern Pacific Main Line Bridge over the Santa Clara River near Montalvo, built in 1914-1915, had developed map cracking similar to the Salinas Valley structures. On June 5, 1933, George W. Rear, M. Am. Soc. C. E., bridge engineer for the Southern Pacific Railroad Company, wrote that the piers showing distress had been built in 1914, using local sand from the bed of the stream, whereas imported sand had been used the following year in constructing the piers which were still in good condition after eighteen years.

Other pavement and structure failures were noted in Los Angeles, Ventura, Santa Barbara, San Luis Obispo, and Monterey counties, where the aggregate was all of the same general type, containing from 4% to 15% total of shale,

cherty shale, and chert. A number of the more important failures were some sections of pavement and sea walls in Ventura and Santa Barbara counties (Fig. 1(c)).

Although the sulfates in sea water undoubtedly contributed to the serious deterioration of the sea walls, it was obvious that this deterioration was accelerated by the infiltration of sea water through cracks resulting from excessive expansion occasioned by other causes. The concrete walls of a school building in Santa Barbara, built in 1931, had cracked to such an extent by 1934 as to require at least partial reconstruction (Fig. 1(d)). All of the failures noted followed the same general pattern and were apparently due to the same underlying cause.

The solution of the problem was complicated by the fact that, although without exception cracking of the nature described was noted only when local fine aggregate had been used, there were numerous instances where the apparently same local aggregate performed in an entirely normal and satisfactory manner.

Immediately north of the pavement failure in Monterey County is a section of pavement, constructed at least six years earlier, in which fine aggregate from the Salinas River was used, but which is still (1940) in excellent condition and shows no evidence of excessive expansion or cracking.

DEVELOPMENT OF TEST PROCEDURE

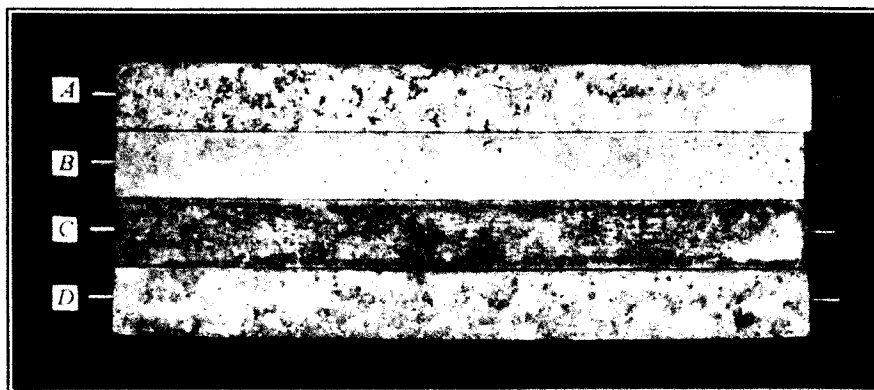
Upon conclusive evidence that the local sand used in the Bradley pavement, constructed in 1936–1937, had played an active part in the failure, a laboratory study was undertaken to determine, if possible, the cause or causes of the trouble and the reason for the inconsistencies that had been noted not only in the locality under immediate investigation, but likewise in all of the coast counties from Monterey to and including the northwesterly part of Los Angeles County.

The first step was to make up mortar and concrete bars of the local (Oro Fino) and the imported (Coyote) fine and coarse aggregates, and then subject some of these bars to continual wetting, some to continual dry exposure, under normal laboratory temperature and humidity conditions, and some to alternate wetting and drying. In one series, after initial curing for seven days, the specimens were dried for three days in an oven at 150° F and then soaked in water at 70° F for four days, the complete cycle taking one week. Another set was dried for two days in the oven at 150° F and soaked seven days in water at 160° F, the complete cycle requiring nine days.

Under none of these curing methods was any excessive expansion observable, even up to more than one year, regardless of the source or nature of the sand, except in the case of a coarse aggregate comprising 100% shale. In that case the expansion was obviously due to a physical expansion of the shale which, when present in large or concentrated quantities, had the effect, ultimately, of rupturing the concrete, but, when present in the normal percentages found in the aggregate under suspicion, had no measurable deleterious effects for the period under observation. In the case of the coarse aggregate with 100% shale, failure occurred on the fifty-first cycle of wetting and drying, at which time the expansion was 0.193%.

AN ACCIDENTAL DISCOVERY

In the meantime, however, upon removing the cover from a 2-in. by 4-in. mortar cylinder which had been cast and retained in a tin container for one year, the specimen was observed to be covered with blotches fringed with a



(a) Relative Length of 1-in. by 1-in. by 10-in. Mortar Bars (Mix 1 : 3)
Cured for Four Months Under Various Conditions



(b) Mortar Specimens (Mix 1 : 2) After Curing Seven Months in Sealed Containers

FIG. 2.—CONDITION OF LABORATORY SPECIMENS AFTER CURING IN AIR, WATER,
AND SEALED CONTAINERS

white efflorescence (subsequently analyzed as sodium carbonate), and in a short time the entire specimen became covered with cracks similar to those shown in Fig. 2(b) and also to the crazing noted in the pavement and other structures in the area under investigation. A similar condition will be noted in

the case of the mortar bars in Fig. 2(a). These specimens are identified, by letters, as follows:

Specimen (see Fig. 2(a))	Curing method	Expansion after four months, in millionths of an in. per in.
A	Sealed container	+7,310
B	Air	-1,350
C	Water	+ 40
D	Sealed container	+7,230

All bars contain the same quantity of high-alkali cement (1.14%) and a neutral aggregate to which was added 10% of the deleterious mineral No. 28039 (see Appendix I).

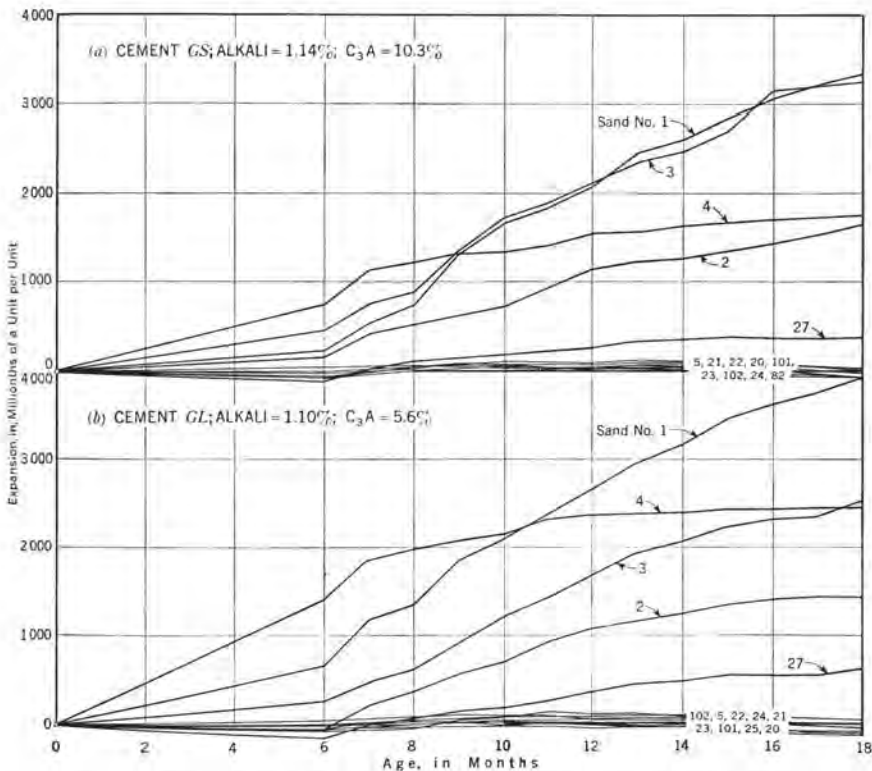


FIG. 3.—EXPANSION OF MORTARS ON CERTAIN CALIFORNIA SANDS AND HIGH-ALKALI CEMENTS OF RELATIVELY HIGH AND LOW C₃A-CONTENT

It was apparent that, when test specimens were kept in sealed containers, or at least protected from the atmosphere and any drying out, but at the same time prevented from any leaching of salts by constant immersion or alternate wetting and drying, a chemical reaction was going on which caused an excessive expansion of the mortar, with ultimate failure.

A series of tests was then started on 1-in. by 1-in. by 10-in. mortar bars cured in sealed containers, as well as in water, and measured for expansion at different ages. Experience with hundreds of specimens, subsequently fabricated, has invariably checked the results accidentally noted in the case of the 2-in. by 4-in. mortar specimen. Bars fabricated with the same sands and the same cement have invariably followed the same expansion pattern.

The local Oro Fino fine aggregate (sand No. 4, Appendix II, and Fig. 3) used in the Monterey County job, in combination with the type of cement used in the work, always shows excessive expansion in a few months (considerable even at twenty-eight days); but the imported (Coyote) sand (No. 20) with the same cement has shown negligible expansion in periods exceeding eighteen months.

In Fig. 3, the specimens were of a 1 : 3 plastic mortar mix, and were cured in sealed containers. The C_3A -content (tricalcium aluminate) does not appear to be a factor in the expansion reactions. Later tests on specimens stored in the moist room, but protected from excess moisture, indicate the same expansion reaction as in sealed containers. However, for the sake of uniformity and convenience, all specimens, other than those constantly wet or dry, were cured in airtight cans.

CURING PROCEDURE

Immediately following fabrication, the test bars are cured twenty-four hours in the moist room under standard conditions. They are then removed from the molds, identified by marking with an indelible pencil, measured, and immediately placed in the containers.

The containers used are regular 6-in. by 12-in. tin cylinder molds with the joints soldered to prevent loss of moisture. The slip cover is probably sufficiently tight to seal the specimens without any other precautions, but if there is any doubt a strip of adhesive tape is wrapped around the joint.

Only enough free water (30 cc to 50 cc) is placed in the bottom of the container to insure keeping the air humid. The specimen rests on the $\frac{1}{2}$ -in. monel metal gage point, and therefore the mortar of the bar is not in direct contact with the water.

Eighteen 1-in. by 1-in. by 10-in. specimens (a day's run) are usually stored in one container. The containers are stored under ordinary room temperature, no special effort being made to keep the temperature constant. The specimens are removed from time to time for measurement and then immediately returned to the containers for further curing and later tests. If rusted badly, the containers are replaced.

CEMENT

Other concrete structures in this area, in which the same type of local sand but a different cement had been used, developed no distress up to five or six years at least. This fact gave rise to the suspicion that the expansion resulted from a chemical reaction between certain ingredients in the aggregate and some ingredients in the cement. Alkali in the cement in the form of the sodium and potassium oxides was suspected and, as the cement used on the Bradley job

contained approximately 1.14% total alkalis, the tests were repeated with another cement low in alkali (0.45%), with definite results, in that there was little, if any, expansion with the low-alkali cement in combination with the local (Oro Fino) sand which had shown so much expansion with the 1.14% alkali cement. The tests have been repeated many times, not only with the two aforementioned cements, but with other California cements of intermediate alkali content and sands from within and without the coast area.

The resultant expansion has almost invariably been proportional to the alkali content of the cement, whenever used in combination with aggregates containing minerals of the deleterious type found in the area under investigation. On the other hand, mortars containing commercial sands originating outside of this area, and containing negligible percentages of shale and chert, being essentially of quartz and feldspar fragments with some granitic and sandstone particles, have developed little, if any expansion, even with high alkali cements.

The data in Figs. 3 and 4 are offered in support of this observation, the mix in each case being a 1 : 3 plastic mortar, and the specimens all being cured in sealed containers. Note that cement *HP* is a puzzolanic type.

Tests on sands Nos. 2 and 4 made after those in Fig. 3 showed expansion as great as, if not greater than, sands Nos. 1 and 3. It would seem, therefore, that the tests in Fig. 3 were influenced either by lack of sufficient moisture to continue the reaction, or by a lower percentage of the deleterious ingredients than in later samples. In fact, these two conditions are probably the cause of some lack of consistency in the tests on other sands, as uniformity of sampling is exceedingly difficult where trouble-causing ingredients are present in such small quantities.

When sand No. 5, Fig. 3, failed to develop excessive expansion, a mineralogical study was made, and it was found that this sample of sand contained negligible percentages of shale, chert, and impure limestone. Therefore, the results are consistent with the nature of the material and confirm the conclusion previously reached regarding the probable source of the trouble.

Within the area under investigation, all of the aggregates from commercial sources, with one possible exception, contain appreciable percentages of shale and chert. All sands with small percentages, or entirely free, of shale and chert show little, if any, expansion up to one year, regardless of the cement used. All sands in the coast area relatively high in shale and chert, on the other hand, develop expansions in a few months roughly in proportion to the alkali content of the cement. In the latter case, negligible expansion is observed in the case of cements with less than 0.5% alkali and high expansion in the case of the 1.14% alkali cement, the other cements ranging in between roughly in proportion to the alkali content (see Fig. 4). Some inconsistencies are noted, but not of such magnitude that they cannot be accounted for by variations in the aggregate.

It is obvious, therefore, that in the presence of certain minerals an otherwise sound but high-alkali cement is a contributing factor to the excessive expansion and subsequent failure of a concrete structure. Under certain conditions this expansion may not be sufficient to disrupt the structure and may cease as soon as the reaction has been completed in any particular cement-

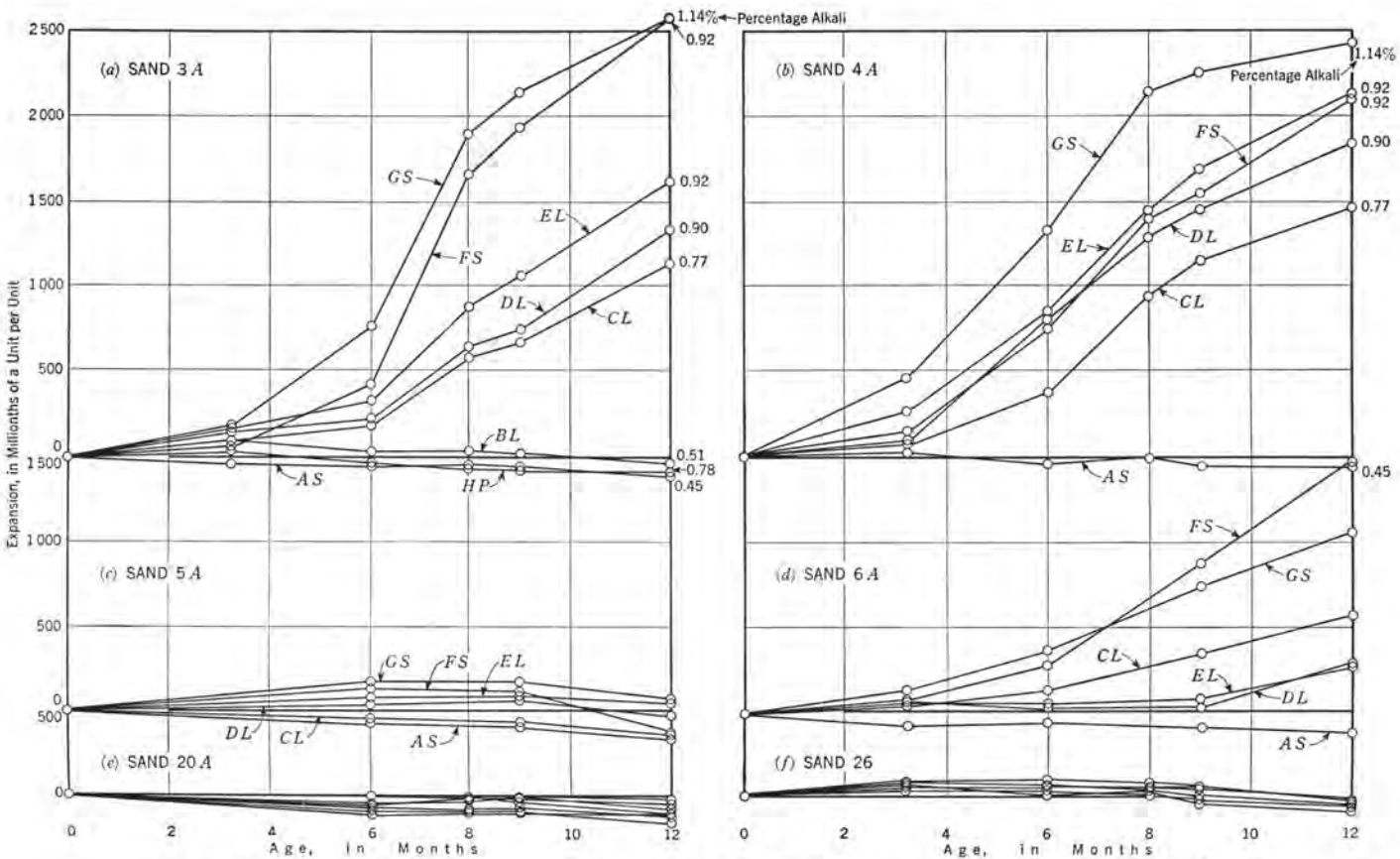


FIG. 4.—EXPANSION OF SAND-CEMENT MORTARS AS INFLUENCED BY THE TYPE OF SAND AND THE ALKALI CONTENT OF THE CEMENT

aggregate combination. In other cases, however, the initial cracking, although above normal but not excessive, may have very serious consequences when the structure is subsequently subjected to attack by sea or alkali waters which, seeping into the concrete mass through fine cracks formed from the primary cause, may take up the work of destruction through corrosion of reinforcing steel or attack on the vulnerable compounds of the cement itself.

AGGREGATES

The coast aggregates included in this study consist of mineral particles predominantly granitic in character with some quartz-feldspar, sandstone, impure limestone, shale, and chert. The granite, quartz-feldspar, and sandstone usually comprise more than 90% of the total; the impure limestone, shale, and chert comprise the remaining 5 to 10%. None of the adverse reactions have been traced to the first group. Some of the minerals in the second group, however, are definitely reactive under appropriate weathering conditions. The minerals in this latter group originate in the Upper Miocene sedimentary deposits. According to Ralph D. Reed,³

"The Upper Miocene in California was a period of widespread seas in which deposition of organic siliceous shale of the Monterey type took place * * *. Whatever conditions are necessary for the deposition of this material prevailed widely during the Upper Miocene from Lower California at least to the Northern Coast Range province and from the San Joaquin Valley area to the present shoreline of the Pacific Ocean."

Many of the types of shale and chert found in the Upper Miocene formations of California are different in several respects from the shale and chert of other geological periods commonly found in other parts of this state and the United States. It has been clearly demonstrated by geologists that the Monterey series of the Miocene, and particularly the Modelo formation, is unique in regard to petrological classification and mineralogical content. Although most of the Modelo formation consists largely of diatomaceous, tuffaceous, and other siliceous shales, many lenses and thin layers of calcareous shale ranging from a fraction of an inch in thickness to a number of feet are intermixed throughout the strata. It is common to find lime, opaline silica, or some chalcedonic silica as the cementing material in the shale. In many cases opaline silica and chalcedony are the main minerals in thin lenses and layers. The opaline silica greatly predominates over chalcedony, but these silicified bands, layers, and concretions have nevertheless been classified as chert by geologists and other authorities on the petrography of the Miocene formations.

The California cherts may be divided into two main classifications: (1) The deleterious cherts of the opaline types, which may or may not contain some chalcedony; and (2) the less questionable group of quartzose particles which includes the red and green varieties of chalcedonic silica such as radiolarian chert of the Franciscan formations, described and named by A. C. Lawson,⁴ as well as jasper and the other varieties of chalcedony. The deleterious particles classified as chert contain opaline silica either in the main or as a

³ "Geology of California," by Ralph D. Reed, 1933, p. 188.

⁴ Geological Atlas, U. S. Geological Survey, San Francisco, Folio 193, 1914.

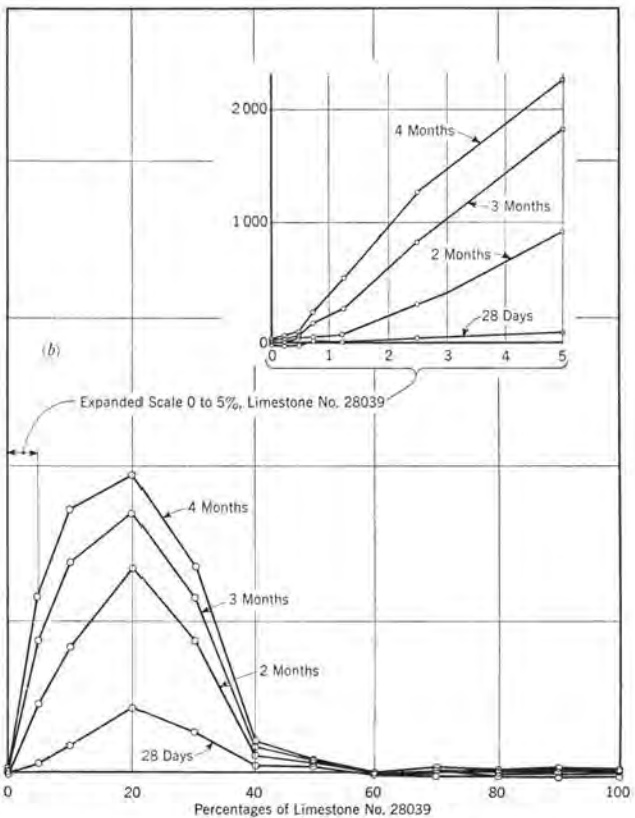
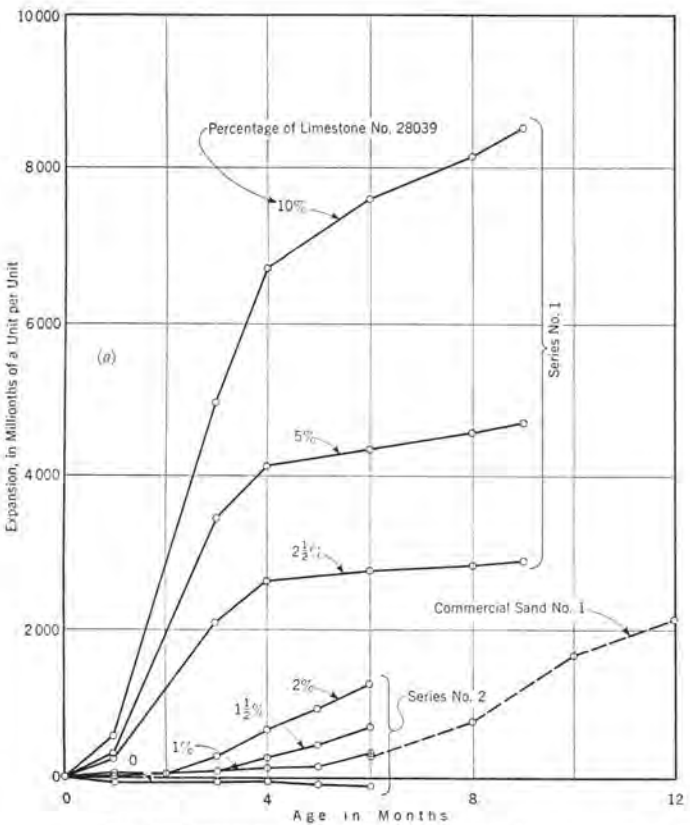


FIG. 5.—COMPARATIVE EXPANSION OF MORTARS CONTAINING SAND NO. 21, IN RELATION TO AGE AND PERCENTAGE OF LIMESTONE NO. 28039

cementing material throughout a shale particle. In the case of particles classified as cherty shale, some of the laminæ contain little or no opaline silica.

Throughout the coast area under investigation, the shale, chert, and impure limestone deposits range from types with negligible percentages of lime and magnesia to a high-lime magnesia shale which in this report is referred to as "siliceous magnesian limestone." This classification is consistent with that given by William Twenhoffel,⁵ who states that:

"The per cent of calcium carbonate or the double carbonate of calcium and magnesium in sedimentary rock ranges from nothing to approximately 100. If the per cent equals or exceeds 50, the rock may be termed a limestone. If the per cent is below 50 the rock should be assigned to some other group. There is, however, no sharp division between limestones and other sedimentary rocks; they grade without sharp break into the sandstones and shales, as well as nearly every other variety of rock."

Rocks covering a wide range from zero to a comparatively high percentage of lime and magnesia have been found in the coast area, and a sufficient number of these rocks have been included in the present study to cover the field fully.

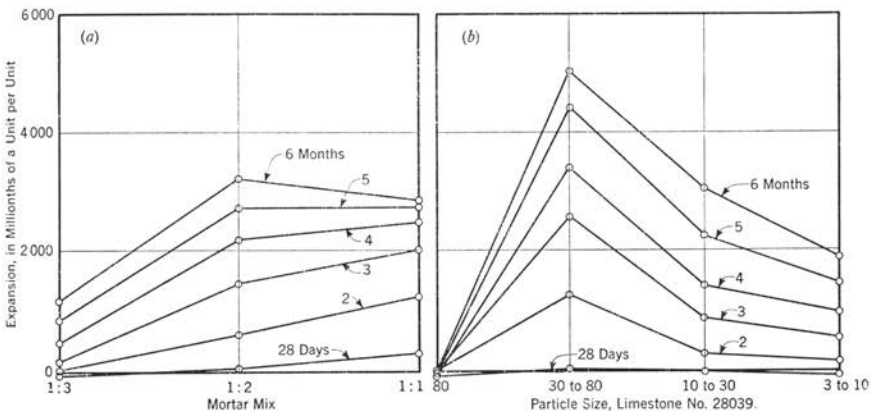


FIG. 6.—COMPARATIVE EXPANSION OF MORTARS CONTAINING SAND NO. 21, IN RELATION TO MORTAR MIX AND PARTICLE SIZE, THE PERCENTAGE OF LIMESTONE NO. 28039 REMAINING CONSTANT AT 5%

An extensive study has been made in an effort to isolate the "bad actors" in the mineral content. Considerable success has attended this effort. Although it appears very probable that some form of hydrous silica plays a very active part, the greatest reaction in the tests described herein has been with material classified as a siliceous magnesian limestone (Nos. 28039 and 28039.A in Table 4, Appendix I), of relatively high specific gravity, low absorption, high sodium sulfate resistance, and low rattler loss. This mineral is one of the most active causes of the trouble, even when present in percentages less than 1.00 (see Figs. 5 and 6). The high-alkali cement GS (Fig. 3) was used throughout. The same aggregate with the low-alkali cement developed no expansion. On the other hand, several of the shales and cherts which expanded moderately in

⁵"Treatise on Sedimentation," by William Twenhoffel, 1932, p. 238.

water showed negligible expansion in sealed containers, even with a high-alkali cement (see Table 1), as contrasted with the siliceous magnesian limestone (No. 28039), which developed no expansion when cured in water but high expansion in sealed containers. It has not been determined if the reaction in the

TABLE 1.—COMPARATIVE EXPANSION OF MORTARS OF SAND No. 21 WITH 10% OF DIFFERENT TYPES OF CRUSHED SHALE CHERT, AND SILICEOUS MAGNESIAN LIMESTONE AND A HIGH-ALKALI CEMENT
(In Millionths of a Unit per Unit)

Age	Mix ^a							
	1 : 3					1 : 2		
	No. 19374	No. 28037	No. 28038	No. 28039	No. 28042	No. 28044	No. 28045	No. 28046
28 days	+90					+55	+ 3	+ 25
2 months						+90	+42	+190
3 months	+238	+18	+47	+1,910	+62	+90	+370	+1,030
6 months	+1,220	- 5	+45	+4,140	+80			
8 months	+2,065	- 3	+35	+5,175	+70			
9 months		-38	- 3	+5,557	+72			
1 year		-90	-37	+6,195	+50			

^a See Appendix I; all these specimens were cured in sealed containers.

case of this impure limestone is due entirely to some form of silica or in part to the magnesium carbonate. If it is due in any part to the magnesium carbonate, the probable chemical reactions in this respect are as follows:

The sodium oxide in the cement hydrates to form sodium hydroxide. The sodium hydroxide, in turn, probably reacts with at least some form of the magnesium carbonate in the siliceous magnesian limestone to form magnesium hydroxide and sodium carbonate; thus:



The sodium carbonate ultimately crystallizes with seven to ten molecules of water, with an increase in volume, and thus causes expansion of considerable magnitude, resulting in stresses sufficient to rupture the concrete. The approximate volume change may be computed theoretically from Eq. 1, assuming the following specific gravities:

Description	Specific gravity
Magnesium carbonate in the rock.	3.037
Sodium hydroxide.	2.130
Magnesian hydroxide.	2.300
Sodium carbonate including 10 molecules of H ₂ O.	1.460

If the molecular weight of the reacting components and the end products are divided by the specific gravities, the following respective volumes are

obtained:

$$\left. \begin{array}{l} \text{Mg CO}_3 = \frac{\text{Molecular weight}}{\text{Specific gravity}} = \frac{84.33}{3.037} = 27.7 \\ + \\ 2 \text{ Na OH} = \frac{80.016}{2.13} = 37.6 \end{array} \right\} 65.3 \text{ (Combined volume of reacting components)}$$

reacts to form:

$$\left. \begin{array}{l} \text{Mg(OH)}_2 = \frac{58.336}{2.3} = 25.36 \\ + \\ \text{Na}_2\text{CO}_3, 10 \text{ H}_2\text{O} = \frac{286.17}{1.46} = 196.00 \end{array} \right\} 221.36 \text{ (Combined volume of reaction products)}$$

or an increase in volume of 239%.

To check the accuracy of this assumption, tests were made to determine the action of sodium hydroxide upon various materials that might be present in the aggregate, such as magnesium carbonate, calcite, dolomite, etc., as well as on the siliceous magnesian limestone.

The method used was to subject the substance under observation to the action of a normal sodium hydroxide solution for seventy-two hours, excluding the possibility of contamination by atmospheric carbon dioxide. A portion of the clear liquid was titrated with normal hydrochloric acid using methyl orange as an indicator. A second volume equal to that used in the methyl orange titration was treated with barium chloride solution to precipitate the carbonates and then titrated with normal hydrochloric acid with phenolphthalein as the indicator. The difference between the volumes of acid used in these determinations was computed to sodium carbonate.

Treated in this manner a sample of:

- (a) Standard calcite yielded only a trace of sodium carbonate as Na_2CO_3 ;
- (b) Bakers calcium carbonate likewise yielded only a trace;
- (c) Dolomite with 7.1% Mg O yielded 1.06% Na_2CO_3 ;
- (d) Technical hydrated magnesium carbonate yielded 51.00% Na_2CO_3 ; and
- (e) The siliceous magnesian limestone with 15.5% Mg O yielded 8.65% Na_2CO_3 .

All material was crushed to pass an 80-mesh screen before test.

These results indicated that sodium hydroxide reacts with certain forms of magnesium carbonate, but not with carbonate of lime. It appears that some similar reaction occurs in the case of at least some of the hydrous silicates. Although some early expansion due to physical causes may be expected from some of the shales, and therefore the percentage of such shales should be held to a reasonable minimum (controlled by the sodium or magnesium sulfate test), nevertheless, when held to comparatively low limits, the expansive force may not be sufficient to cause rupture except in the nature of popouts when particles are close to the surface. This conclusion is confirmed by observation of numerous structures which, except for surface popouts, show no distress over a

period of years even if the aggregate contains a relatively high percentage of many of the types of shale found in the area under investigation. With some cherts and shales, however, in addition to the siliceous magnesian limestone, a chemical reaction of a decidedly destructive nature always takes place in the presence of a high-alkali cement.

An astonishing development was the effect of a very small percentage of the high lime-magnesia rock. As will be seen by reference to Fig. 5(a), as low as 1.00% of this mineral caused considerable expansion in six months, the expansion in that period being almost identical with the expansion mortars of sand No. 1 in the same period of time, indicating that sand No. 1 contains not more than 1.00% of deleterious particles but that even this low percentage is objectionable.

The particle size of this mineral also has an important bearing on the result. It was thought that, by crushing the deleterious particles to pass 200-mesh completely, an accelerated reaction might be had. The reverse was the case, as specimens fabricated with -80-mesh particles developed no expansion in sealed containers, whereas the -30-mesh to +80-mesh particle specimens showed the greatest expansion (see Fig. 6(b)). Therefore, it appears that the reaction between the reactive ingredient in the aggregate and the alkali in the cement, when the aggregate is in a finely divided state, is either dissipated throughout the mass in such a way as to cause no high expansive forces or the reaction is largely over before the concrete attains permanent set. One theory is that the expansion is taken up in the interstices and by the gel, thus reducing the measurable manifestation of the reaction to negligible proportions.

MERRIMAN ALKALINITY AND FREE ALKALI TEST

The Merriman test⁶ for alkalinity and free alkali was applied to the cements, but it was found that this test was not always consistent with the results. One cement, relatively low in the Merriman test, but with high alkali as determined by chemical analysis, developed high expansion; and its action, therefore, was consistent with the total alkali as determined from the chemical analysis rather than with the percentage of soluble alkali as determined by the Merriman test. Another cement with a high Merriman test, but low in alkali as determined by the chemical analysis, gave low expansion results. The reason for the discrepancy appears to be that the soluble portions of some cements go into solution much more slowly than others. The conclusion has been reached, therefore, that the Merriman test procedure, in its present form at least, is not suitable for a proper classification of cements in the order of the reactions encountered in the California tests.

EXTENT OF TESTS

Tests have been made on fine aggregate from all of the commercial sources within the region affected and from several sources outside of this area for comparison purposes; they have been made also on most of the commercial cements manufactured in California ranging in alkali content from less than 0.50% to approximately 1.14% (Table 5, Appendix III).

⁶ Specifications for Cement, Board of Water Supply, City of New York.

As previously stated, negligible expansion developed with sands from outside the affected area. With one exception, all of the local sands showed high expansion in proportion to the alkali content of the cement. With the exception of the one sand, all of the samples contained from 5% to 10% of shale, chert, and the siliceous magnesian limestone. The sample of sand (sand No. 5) from the one deposit which failed to react was subsequently analyzed and found to contain only a very small percentage of the deleterious particles.

Numerous combinations have been made of aggregate from all commercial deposits and cement from most of the California mills. For check purposes, the study has been expanded to include, also, several cements from other parts of the United States.

Following a visit to the laboratory, when he was in California during the summer of 1939, the late Thaddeus Merriman, M. Am. Soc. C. E., who was much interested in the study, forwarded a sample of low-alkali cement (0.47%) from a Lehigh Valley plant (cement *N* in Table 5, Appendix III); and Ira Paul of the New York State Highway Department furnished a sample of 0.64% alkali cement from a New York plant (cement *R*). Through F. V. Reagel of the Missouri State Highway Department and W. E. Gibson, Assoc. M. Am. Soc. C. E., of Kansas, cements were secured similar to those used in pavements in Missouri and Kansas (cements *M* and *O*). These out-of-state cements have all been tested in combination with the Oro Fino and Coyote sands.

The expansion reactions have paralleled the reactions of the California brands. Cement *M* with a high-alkali content (0.83%) has developed excessive expansion with the Oro Fino sand (4,010 millionths of a unit per unit in fourteen months) and negligible expansion with the Coyote sand, whereas cements *N*, *O*, and *R*, comparatively low in alkali, have developed little if any expansion with either the Oro Fino or Coyote sands.

More than 3,000 1-in. by 1-in. by 10-in. mortar specimens of all combinations were fabricated and tested for expansion under different curing methods. The present status of knowledge of the subject was only arrived at through following numerous leads, some of which led into blind alleys and others of which were productive of results pointing the way and suggesting additional tests or lines of investigation.

Series I.—This series was started in May, 1938, and included only the two sands used on the Bradley job. Several coarse aggregates were used, including chert, shale, granite, and an altered dacite.

The cements in this first series were of the brand used in the Bradley job (a high-alkali cement) and in addition a low-alkali cement from another mill. The test specimens consisted of 2-in. by 2-in. by 11½-in. bars of six-sack concrete, using 50% sand and 50% coarse aggregate, and the maximum size was ¾ in. One set of bars was cured in water, one set in air, and other sets alternately soaked and dried at air and water temperatures ranging from 70° F to 160° F. These tests produced no results of value, even up to one year, and at no time duplicated field experience with the local fine aggregate and job cement.

All specimens cured in water showed a slight expansion in the earlier period, but by 200 days all showed shrinkage from the peak length. At one year all specimens were shorter than the original length with the exception of the shale

coarse aggregate specimens (ledge shale from Oro Fino Canyon), which showed a slight expansion (0.009%).

All specimens cured in air at laboratory temperature showed shrinkages ranging from 0.1% to 0.3%, but no cracking. In the alternately wet and dry group, there was shrinkage or negligible expansion with the exception of the coarse aggregate specimen of 100% shale which, by the fifty-first cycle, had expanded 0.193% and failed by cracking.

Series IA.—Shortly after Series I was started, supplementary specimens of the same size were placed under similar test, using aggregates from various spots in the Oro Fino deposit, and also from other commercial sources throughout the district between Monterey and Los Angeles counties. Again the results were negative.

Series II.—After Series I and IA had been under way approximately three months, the condition of the 2-in. by 4-in. mortar specimens cured in a sealed container was observed, and a new series was immediately started, the specimens in this series being fabricated in September and October, 1938. Because of the expense and labor involved in fabricating and measuring concrete specimens, and because it was apparent from an inspection of the mortar specimen cured in the sealed container that the fine aggregate was considerably more reactive, at early stages at least, than the coarse aggregate, Series II consisted of fine-aggregate mortar specimens only, and the specimens in all subsequent series, except one, were mortar specimens. At the start, six 1-in. by 1-in. by 10-in. 1 : 3 mortar bars were fabricated from each mix for curing under different conditions, and the results reported are the average of several specimens. As the 1 : 2 mortars were found much more reactive, all later specimens were fabricated from this mix.

Sands from fourteen sources were included in Series II—five from commercial sources throughout the affected area; seven from outside sources, free of shale and chert; and in addition a crushed diorite and a crushed quartz. With little information at that time relative to the most probable source of the trouble, and to ascertain if the situation could be corrected by the use of a low C_3A cement, two types of the brand of cement used on the Bradley job were included: (1) The job cement with 10.3% C_3A and 1.14% alkali, and (2) a modified cement from the same mill containing 5.6% C_3A and 1.10% alkali. To hold the amount of testing to a minimum, no other cements were included in Series II.

The mixes were put up in duplicate, one set with the high-alkali and comparatively high C_3A , and the other with the high-alkali and comparatively low C_3A cement. A uniform water-cement ratio (0.94) was used, the slump varying $1\frac{3}{4}$ in. to $2\frac{3}{4}$ in. with the natural sands, 1 in. to $1\frac{1}{4}$ in. for sands having rock chips in the coarser sizes, and $\frac{5}{8}$ in. to $1\frac{1}{4}$ in. for the crushed quartz and diorite. Some of the specimens were cured continuously in water, some in air, some alternately wet and dry, and some in sealed containers in the presence of a slight amount of free water.

As no material reaction was expected short of six months, the sealed containers were not opened or the specimens measured until six months had elapsed. The reaction was found to be so extensive by this time (Fig. 3) that in all

subsequent series the measurements were started at earlier periods. After measuring, the specimens were returned to the sealed containers for further curing and measurement at subsequent test periods, usually monthly. At six months all of the sands from the shale-chert infected area, except one, showed considerable expansion. The exception was the sand which was subsequently found to be low in shale and chert.

All of the sands from outside the infected area, except one (all of which have a good construction history), showed either only a slight expansion or a shrinkage at six months. This relative condition has persisted throughout the entire test period to date. The expansion of the one exception (No. 27 in Fig. 3) was not especially high, but, as it was decidedly out of line with the others, a thorough study is being made (1940) to ascertain the cause.

Mortar cylinders (2 in. by 4 in.) for compression tests, fabricated from the same mixes as the bars and cured in water, developed equal strengths up to one year for the poor and the good sands. Later specimens cured in sealed containers showed a gradual falling off in strength with age whenever the infected sands were used.

Series III.—As soon as Series II was well under way and time permitted, a third series was started similar to Series II, but including a number of other California brands of cement ranging from low to high alkali. In addition to the bars, 2-in. by 4-in. mortar cylinders were cast and cured in sealed containers for breaking at twenty-eight days, six months, and one, two, and five years.

As in the previous series, all bars cured continuously in water expanded slightly at first and then began to shrink. The first expansion measurements of the specimens cured in sealed containers were made at one hundred days. Even at that period, considerable expansion was noted in the case of the infected sands.

Series IV.—Having determined definitely from Series II and III that certain sands were reactive, the next step was to determine, if possible, which mineral ingredient or ingredients in the sands were the source of the trouble. Since all minerals except the shale and chert had been removed from suspicion by previous tests on selected sands, four suspected minerals were selected from the infected area, including a diatomaceous shale (No. 28037); a chert (No. 28038); and a calcareous shale (No. 28039), later classified as a siliceous magnesian limestone (Table 4, Appendix I). These shales and cherts were crushed to pass a No. 3 screen and were combined in various percentages with a neutral sand (No. 21) from the Russian River, north of San Francisco Bay.

This series was later expanded to include a serpentine found in the coast area, a calcareous shale (No. 19374) with approximately 6% Ca O but low magnesia, a siliceous chert (No. 19375), and two opaline cherty shales (Nos. 28045 and 28046). An opal and an opalized chert were likewise included to determine the effect of an opaline silica. Crushed limestone was used in other specimens.

The conclusion from this test was that the principal ingredient in the sand contributing to the abnormal volume change was the "siliceous magnesian limestone" and that probably the magnesia in the form of $Mg CO_3$ in this rock was one of the active reagents with the sodium hydroxide from the sodium oxide

in the cement. However, excessive expansion was not confined to the specimens of No. 28039 but was likewise noted, although to a lesser degree, with the laminated calcareous shale No. 19374, and the opaline cherty shales Nos. 28045 and 28046 (Table 4, Appendix I).

The early tests in this series were made with 2.5%, 5%, and 10% additions to the Russian River sand. As evidence accumulated that excessive expansion occurred with even as low as $2\frac{1}{2}\%$ of No. 28039, the series was expanded to include specimens with lower percentages ranging down to as low as 0.10% (see Fig. 5(a)).

OTHER TESTS

Later test series have included observations to determine the effect of:

- (1) Age of cement;
- (2) Washing soluble salts out of the cement, treating the aggregate with this resultant liquor, and then testing for expansion;
- (3) Admixtures such as pumicite, celite, ground Ottawa sand, calcium chloride, and Vinsol resin;
- (4) Treating the sand with sodium hydroxide and dilute hydrochloric acid;
- (5) Varying the quantity of cement, using 1 : 3, 1 : 2, and 1 : 1 mortar mixes; and
- (6) Methods of accelerating reaction by heating so as to reduce the time of test.

Most of these later tests have not been conducted long enough to produce conclusive data of value. Apparently, however, the test cannot be accelerated by heat, by the autoclave, or by pulverizing the deleterious materials, but can be accelerated by using 1 : 2 mortar mixes instead of 1 : 3 and adding from 5% to 20% of the reactive minerals crushed and screened to the size range, a -30-mesh to +80-mesh size.

The addition of a pozzolanic material seems to be effective, as 25% pumicite substituted for an equivalent weight of high-alkali cement reduced the expansion to a negligible amount at early periods. Part of the reduction may have been due to the lower percentage of total alkali in the combined mix. Ground Ottawa sand, however, was much less reactive and calcium chloride had little effect (see Fig. 7). The reaction with the pozzolanic-type cement included in Series II (*HP* in Fig. 4) was likewise considerably less than with other standard cements of the same or less alkali content. Vinsol resin appears effective to a certain extent.

Treating the Oro Fino sand with water mixed with, and then leached from, a high-alkali cement, or with a solution of sodium hydroxide, apparently stops any subsequent reaction; but treating with a hydrochloric acid solution is ineffective. This would indicate that it may be some form of silicate rather than carbonate which causes the trouble.

CONCRETE TESTS

With the exception of Series I and IA, all of the tests described were made on mortar specimens. A later series consisted of 6-in. by 6-in. by 30-in. speci-

mens of six-sack concrete, using different combinations of good and bad coarse and fine aggregates. Specimens of each mix were cured, sealed in water, and were kept continuously dry at laboratory humidity and temperature. This test has been in progress too short a time, however, to produce information of value.

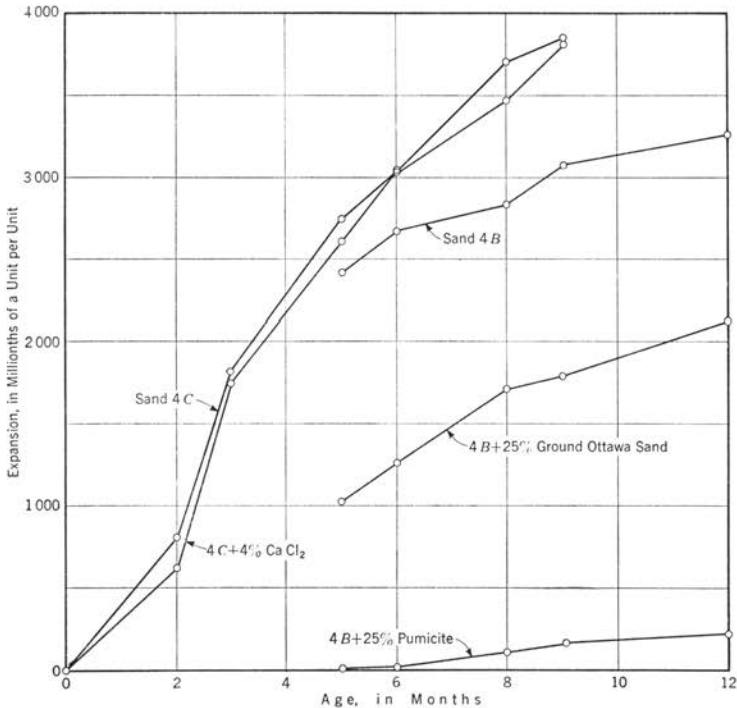


FIG. 7.—EFFECT OF VARIOUS ADMIXTURES ON THE EXPANSION OF A HIGH-ALKALI CEMENT AND REACTIVE SAND MORTAR (1 : 3 MIX)

SHALE AND CHERT POPOUTS

Although the laboratory investigations described herein conclusively demonstrate a very destructive chemical reaction between a high-alkali cement and some ingredient in the siliceous magnesian limestones, nevertheless one cannot overlook the fact that some chemical action is also taking place in the presence of some types of the low lime-magnesian shales and cherts, as evidenced by the data shown in Table 1, as well as by a study of the extensive popouts observed in numerous structures, including pavements, bridges, and buildings where shale or chert particles are invariably found at the base of the popouts, frequently accompanied by a soft viscous substance analyzed as a silica gel with some form of sodium silicate. Figs. 8(a) and 8(b) are views of large popouts from the basement of the old Times Building in Los Angeles. Fig. 8(a) is a part of a 5-in. popout showing at: (a) Sodium silicate gel; (b) an intermediate zone of partly altered shale; and (c) apparently unaltered rock. The chemical analyses

of these samples, given in Table 2, were necessarily made on very small specimens and may therefore be inaccurate in some details. Fig. 8(b) shows altered and unaltered parts of the mineral that caused the popout.

The aforementioned silica gel frequently has been observed exuding from cracks or pores in the face of concrete structures in which aggregates and ce-

TABLE 2.—CHEMICAL COMPOSITION OF ROCK AND GEL FOUND IN THE TWO TYPICAL POPOUTS SHOWN IN FIGS. 8(a) AND 8(b)

Description (1)	Formu- la (2)	FIG. 8(a)				FIG. 8(b)	
		Gel (3)	Inter- mediate altered shale (4)	Apparently Unaltered Rock		Gel (7)	Apparently unaltered rock (8)
				Upper layer (5)	Lower layer (6)		
Moisture.....		12.63	8.92	3.12	3.23	9.69	3.38
Combined H ₂ O and organic matter..		9.81	5.84	2.80	3.41	6.96	5.00
Iron.....	Fe ₂ O ₃	2.40	1.92	3.83	3.83	3.19	2.55
Aluminum.....	Al ₂ O ₃	4.38	5.84	1.09	6.37	4.61	4.69
Lime.....	Ca O	2.90	2.36	0.92	2.50	2.62	1.36
Magnesia.....	Mg O	0.58	0.72	0.54	1.09	0.85	0.79
Alkalis.....	Na ₂ O	12.93	9.62	2.04	4.90	12.77	5.00
Carbon dioxide.....	CO ₂		2.50	0.71	1.43	3.93	1.79
Chlorides.....	Cl		0.72	0.40	0.24	0.48	0.16
Silica.....	Si O ₂	53.86	60.16	83.30	71.22	53.40	74.00
Undetermined.....		0.51	1.40	1.25	1.78	1.50	1.28
Total.....		100.00	100.00	100.00	100.00	100.00	100.00

ments similar to those under investigation had been used. This type of gel has also been found throughout the cores and pieces of concrete examined from all of the failed pavements and structures. In some cases a number of aggregate particles had entirely altered to gel, so that it often swelled out above a freshly cut surface of a concrete specimen. In many cases the reaction has only partly progressed into particles identified as siliceous shales or cherts of a type relatively free from lime and magnesium carbonates. Although the gel has usually been found in a plastic state in fresh popouts, and in specimens cut from beyond the exposed surfaces of the concrete pavements and structures, it hardens readily and shrinks when dried on exposure to the air.

A detailed examination was made of approximately 200 popout and core specimens removed from the affected buildings, sea walls, bridges, and pavements over an area extending from Los Angeles on the south to the northern part of the Salinas Valley. As defined by Allan H. Nicol, mineral technologist for the State Division of Highways, each popout particle had associated with it a considerable amount of optically isotropic material of very low index of refraction. This material was identified as opaline silica with complex sodium silicates and was found to have indexes ranging from 1.41 to 1.54. This substance, which was slightly plastic before drying, is hereafter referred to as "gel." It was found that the index of refraction of the dried gel increased with the color. The clear, glassy variety had indexes ranging from 1.41 to 1.47.

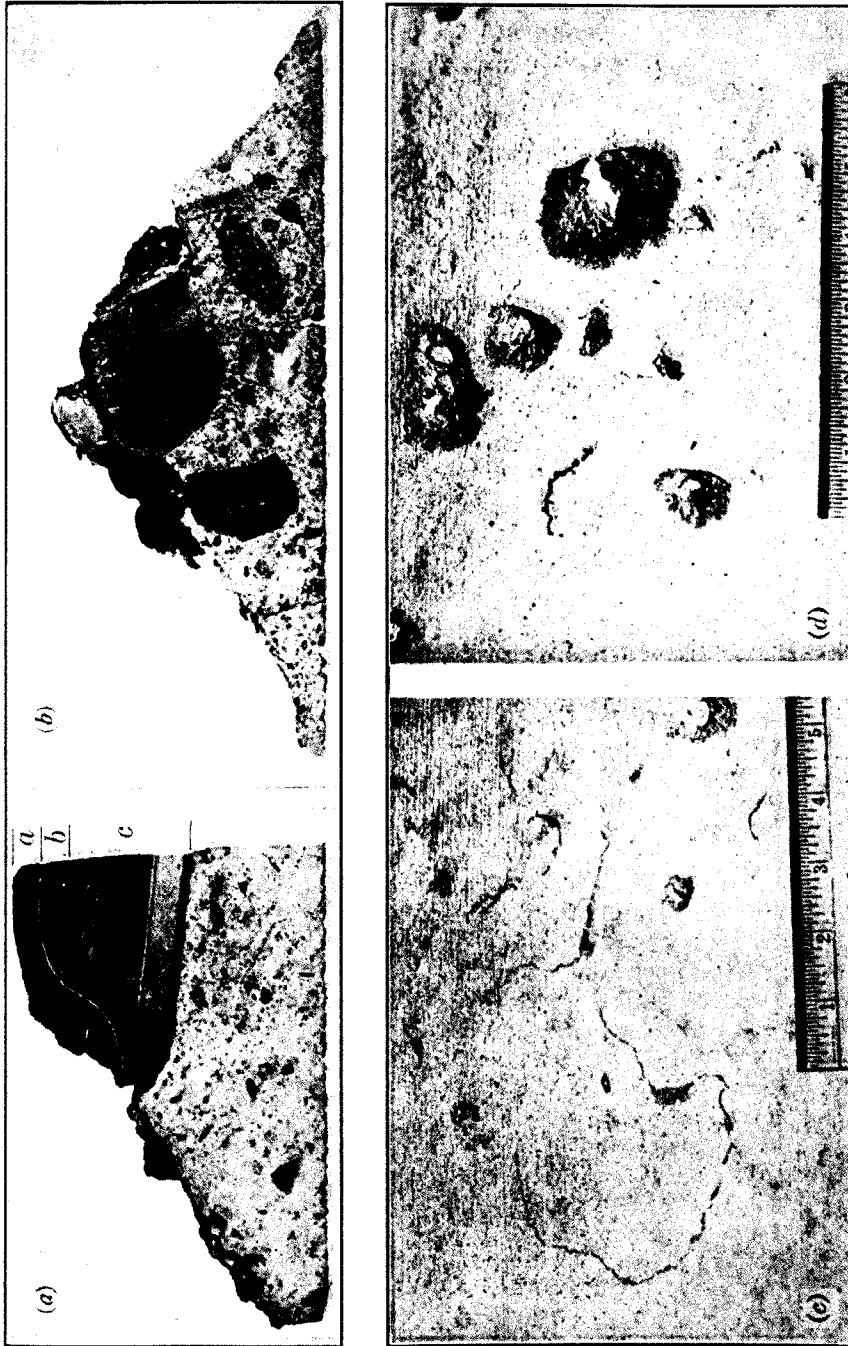


FIG. 8.—TYPICAL SHALE POPOUTS

The yellow and pale brown types showed values from 1.46 to 1.49, whereas with the brown to dark brown types the values ranged from 1.47 to 1.54.

Microchemical tests showed that the type of gel with a low refractive index was a nearly pure opaline silica, relatively free from sodium, magnesium, aluminum, calcium, and iron salts, whereas the yellow, amber, and brown varieties, which predominated in many specimens, contained increasing percentages of silicates and other compounds of these and other elements. The presence of these compounds, together with a variable content of adsorbed water, undoubtedly could account for the variable refractive indexes.

Most of this gel is fluorescent under ultraviolet light. A strong fluorescence was observed in the expansion bars and mortar cylinders which carried various percentages of No. 28039 (siliceous magnesian limestone; see Appendix I). These specimens had been subjected to the sealed curing test. The fluorescence in this case is due to gel derived from the particles of No. 28039 in the aggregate, as the rock in its original unaltered condition does not fluoresce.

The gel-like material associated with these specimens contains opaline silica, with varying amounts of sodium, magnesium, aluminum, calcium, and iron compounds. All of the gel examined on popouts, and in the cores and broken concrete from the various sources, shows similarity of optical properties and chemical composition.

Siliceous, calcareous, and cherty shales were the principal petrographic types associated with the popouts and the gels found in the concrete specimens. Chert was also commonly found, but it was impossible to determine how many of the completely altered particles may have been chert before the reaction.

The dark gel carrying the impurities was usually associated with a dark-colored, organic, siliceous shale or chert. The light-colored gel was normally found with light-colored shale or chert, usually cream, tan, or buff. These light-colored shales and cherts were generally more free from organic material and fossil remnants than their dark-colored equivalents.

It can be reasoned that this substance forms in the presence of moisture through the action of alkali in the cement or possibly in the rock on some form of silica in the rock, resulting in a gel-like end product consisting primarily of opaline silica, sodium silicates, and water. As a partial proof of this assumption, white deposits or incrustations containing more than 50% Na_2CO_3 have been found on the protected parts of structures where neither surface water nor ground water could come directly in contact with the concrete surface on which the deposit occurred. Presumably this sodium was in the form of sodium hydroxide in the concrete and was changed to sodium carbonate by carbon dioxide derived from the air.

Following this reasoning, mineralogy has well established the fact that hydrous forms of silica, such as opaline, are readily dissolved in either sodium or potassium hydroxide solutions, and also that these forms of silica are found in abundance throughout some of the Miocene formations in the area under discussion. All siliceous shales and cherts, therefore, are subject to question, in connection with the chemical reaction resulting in the gel substance. Extensive tests show that many types of shale and chert found in the gravel deposits are readily dissolved and disintegrated by soaking in a 10% solution of sodium

hydroxide. In Fig. 9 the effects of soaking are shown for two materials—specimens cut from ledge rock, and $\frac{1}{2}$ -in. shale and chert particles from stream-bed gravel deposits.

Although these tests show only that the gel type of chemical action accompanying popouts and expansion failures can be approximately duplicated in the laboratory by the use of a sodium hydroxide (Na OH) solution, additional tests indicate that a similar action occurs when these types of aggregate are soaked in the mixing water from high-alkali cements. The chemical composi-

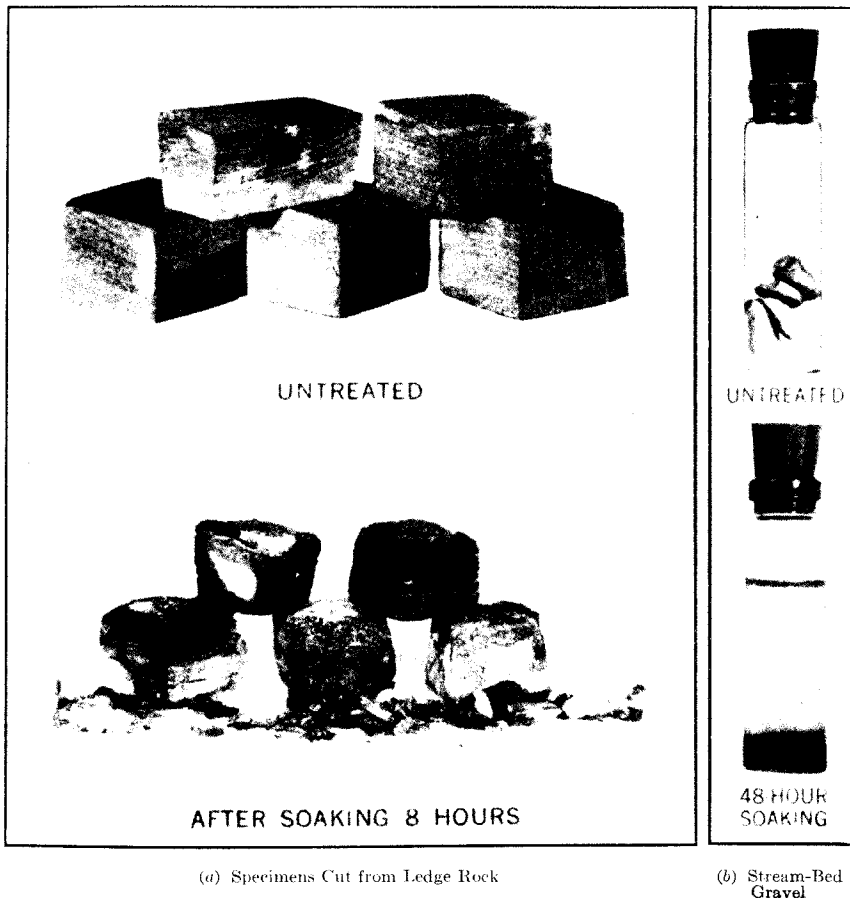


FIG. 9.—EFFECT OF A 10% SODIUM HYDROXIDE SOLUTION (AT 70° F) ON SOME TYPES OF SILICEOUS (CHERTY) SHALE AND CHERT FROM THE CALIFORNIA MIOCENE FORMATIONS

tion of water containing alkali, leached from a low-alkali (0.45%) and a high-alkali (1.14%) cement, is shown in Table 3, together with the change in each solution, after digesting for 120 hr at 200° F with Oro Fino sand containing about 9% of chert and shale particles. It is significant that the water from the

high-alkali cement dissolved approximately ten times more silica during the treatment than the water from the low-alkali cement.

Figs. 8(c) and 8(d) show two typical popouts of the type accompanied by relatively large deposits of gel. It will be noted from Table 2 that these shale

TABLE 3.—CHEMICAL COMPOSITION OF WASH WATERS FROM A LOW-ALKALI AND A HIGH-ALKALI CEMENT AND THE SAME SOLUTIONS AFTER DIGESTING FOR 120 HR AT 200° F WITH ORO FINO SAND CONTAINING ABOUT 9% OF SHALE AND CHERT PARTICLES (In Parts per Million)

Description	Cl	CO ₂	H CO ₃	OH	SO ₃	Si O ₂	Al ₂ O ₃ (Fe ₂ O ₃)	Ca O	Mg O	Na ₂ O*
WASH WATER FROM:										
Low-alkali cement.....	20	75		1,400	10	7		450		2,200
High-alkali cement.....	60	240		3,200	36	39		110		6,000
SOLUTIONS AFTER DIGESTING WITH SAND: ^b										
Low-alkali cement.....	4	250		870	23	590	42			1,800
High-alkali cement.....	50	660		2,800	45	6,100				5,600

* Alkalies (Na and K) reported as Na₂O.

^b 3-mesh to 10-mesh sand particles.

particles have chemical compositions somewhat similar to No. 28042 (Table 4, Appendix I), particularly in regard to lime, magnesia, and alkali, although the shale in Figs. 8(a) and 8(b) is very much harder than that in Figs. 8(c) and 8(d), or the soft shale represented by No. 28042. Even if the gel type of reaction accompanies many popouts and other expansion failures observed in the field and also can be accounted for, at least theoretically, when a high-alkali cement is used, the volume change and the exact source of the stress causing the popouts and accompanying the reaction require further investigation.

CONCLUSION

The tests described herein justify the following conclusions:

1. Certain mineral constituents in concrete aggregates contribute to expansion of concrete and sometimes develop stresses of such magnitude as to cause failure.

2. Some shales expand excessively when saturated with water or when they are alternately wet and dry and, therefore, the percentage of such material should be kept to a practical minimum. This action, however, appears to be physical and of much less intensity than a chemical reaction with other minerals.

3. Excessive expansion, sufficient to rupture a concrete mass, may occur when certain minerals are present. The reaction in this case is chemical, and evidence indicates that it always takes place with the siliceous magnesian lime rocks found in the aggregates from the Upper Miocene sedimentary deposits of the state and frequently in the presence of some of the low-magnesia, low-lime shales and cherts.

4. The chemical reaction producing excessive expansion apparently occurs only when the portland cement component contains an appreciable percentage of alkali in the form of sodium and potassium oxides. It is of an intensity proportional to the percentage of such oxides, apparently being of such low order as to be negligible when the alkali content is less than 0.6%.

ACKNOWLEDGMENTS

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APPENDIX I

MINERAL IDENTIFICATION

The chemical analysis and physical properties of a few of the Miocene shales, cherts, and impure limestones, found in the coast area between Monterey and Los Angeles, Calif., are given in Table 4. Each sample is identified by a laboratory test number that identifies the following detailed description of each one:

No. 19374—Laminated Calcareous Shale:

Groundmass an impalpable mixture of clay, opaline silica, and sericite, carrying abundant fragments of quartz, orthoclase, chalcedony, and calcite, with some marcasite. Organic matter and fossil relics, including foraminifera and diatoms, are found occasionally as stringy accumulations parallel with the laminæ. The chalcedony occurs chiefly as fragmental grains, with an occasional veinlet. A few small clay lenses were observed without any appreciable embedded mineral grains of sufficient size to be identified. The laminations in this rock are quite high in clay and opaline silica, and carry the thickest layers of organic matter and fossils. This could explain the ease with which this material splits apart.

No. 19375—(Chalcedonic) Cherty Shale:

Predominant evidence of chalcedonic replacement of the shaly portions of this rock. The groundmass is predominantly chalcedony of the flamboyant type, with some areas not entirely replaced. Sizable fragments of recognizable minerals are lacking. Organic matter, low in content, occurs in layers that tend to parallel the bedding. The entire specimen is pierced throughout by chalcedony veinlets. Quartz and feldspar fragments are lacking. Opaline silica not observed in this material. Fossils absent.

TABLE 4.—CHEMICAL ANALYSIS AND PHYSICAL PROPERTIES OF SHALES,
CHERTS, AND LIMESTONES
(All Values Are Percentages)

No.	Description	Formula	LABORATORY TEST NOS.:			
			19374	19375	28037	28038
1	Moisture		0.75	0.22	3.88	2.14
2	Organic matter ^a		1.42	0.98	2.21	2.63
3	Iron	Fe ₂ O ₃	3.38	2.64	2.59	2.59
4	Alumina	Al ₂ O ₃	1.40	3.15	13.11	0.79
5	Lime	Ca O	6.01	0.65	2.71	Trace
6	Magnesia	Mg O	0.60	0.51	1.69	Trace
7	Alkali	Na ₂ O	0.58	0.78	2.11	1.43
8	Manganese	Mn ₂ O ₃	0.01	0.03	0.36	
9	Carbonates	CO ₂	9.46	0.68	2.31	
10	Undetermined		0.69	0.14	0.61	0.48
11	Silica	Si O ₂	75.70	90.22	68.42	89.94
12	Totals		100.00	100.00	100.00	100.00
13	Average loss, Na ₂ SO ₄ (percentages)		22.0		36.4	28.7
14	Rattler Test: ^b					
15	100 revolutions		5.2		8.0	9.4
16	500 revolutions		23.0		31.2	34.6
17	Specific Gravity:					
18	Le Chatlier				2.20	2.00
19	Saturated surface dry		1.82		1.80	1.89
20	Absorption:					
21	Percentages		8.0		10.2	4.3

TABLE 4—(Continued)

No.	28039	28039A	28042	28045	28046	30704
1	0.42	0.92	3.92	4.74	5.09	3.8
2	4.15	0.58	3.12	Trace	2.19	8.3
3	0.83	0.99	3.24	3.19	3.52	1.1
4	0.27	1.22	12.40	5.09	3.90	3.5
5	26.24	30.85	1.80	5.18	3.58	0.4
6	15.55	8.75	1.33	0.52	0.52	Trace
7	0.20	0.53	4.21	2.09	1.87	
8	0.02					
9	33.92	37.03	0.44	2.50	2.30	
10	0.58	0.39	0.84	0.44	0.66	1.6
11	17.82	18.74	68.70	76.25	76.37	85.1
12	100.00	100.00	100.00	100.00	100.00	100.00
13	2.8		72.7	56.3	48.2	
14	4.8		11.2	10.2		
15	20.0		41.8	36.0		
16	2.62		2.50	2.28	2.16	
17	2.43		1.90	1.94	1.94	
18	1.7		7.1	8.4	7.7	

^a Combined water and organic matter.^b Los Angeles Rattler Test.

No. 28037—Diatomaceous Shale (Soft Siliceous Type):

Carries a few fragments of plagioclase and quartz. Groundmass consists chiefly of diatoms and other opaline material, together with clay, some mica (probably sericite), and a variable amount of organic matter. Groundmass is quite uniform.

No. 28038—Chert:

Opaline material, with some organic matter, and a few fine chalcedony fragments constitute the groundmass of this specimen. The groundmass is pierced throughout the entire length of the slide by a series of fine chalcedony veinlets that average about 0.15 mm in width. These veinlets

are all more or less parallel with each other and are apparently conformable with the bedding. They also parallel the heavy layers of organic matter. Abundant evidence of chalcedonic replacement throughout groundmass. "Canals" or veinlets are in portions partly opaline. No fossils or diatoms were noticed. Chalcedony of veinlets is of flamboyant type and carries minute opaque inclusions, possibly marcasite. Many canals or veinlets not entirely sealed from wall to wall by opaline cement, leaving innumerable fissures and openings.

No. 28039—Siliceous Magnesian Limestone:

A groundmass composed principally of chalcedony, opal, dolomite, and calcite. The dolomite occurs as rhombohedrons; calcite shows excellent twinning lamellæ; the chalcedony is flamboyant and shows aggregate polarization under *X* nicols. A few diatoms present in the groundmass, many showing replacement by calcite, dolomite, or chalcedony. Irregular patches of organic matter, concentrated near the chalcedony.

No. 28042—Soft Shale (Santa Margarita Formation):

Quartz and other mineral grains are very abundant in this material (over 25% of groundmass). Groundmass carries abundant organic matter and finely disseminated marcasite. No evidence of siliceous replacement. No diatoms or other micro-fossils observed. Cracks and fissures numerous. Cement of groundmass chiefly clay. No evidence of recrystallization—hence, material is probably quite soft and friable. Average size of grains approximately 0.039 mm. Consist principally of quartz, with some plagioclase and actinolite. Quartz has inclusions, possibly rutile. Organic matter strung out parallel to laminæ. This sample also carries a considerable amount of an anisotropic, pleochroic mineral (index greater than balsam) found in popouts.

No. 28045—Opaline Cherty Shale:

This rock shows strong similarity to No. 19374 and to No. 28046, under low-power magnification. It is of the same geological age as No. 19374 and No. 28046, as evidenced by the foraminifera and other fossils, which show partial chalcedonic replacement. The groundmass appears to be an intimate mixture of chiefly opaline silica with a small amount of diagenetic glauconite and clayey portions, with traces of organic matter. The latter is of fairly uniform distribution throughout the slide. Embedded in this groundmass are abundant coarse detrital grains of quartz, orthoclase, and plagioclase. Numerous feldspars appear partly glauconitized. Chalcedony is not very abundant in the groundmass, except as a replacement of the fossils. No free calcite or dolomite as fragments or veins was observed. This material differs from No. 19374 by a lower calcite-dolomite content, and by a higher amount of detrital quartz and feldspars, as well as a more uniform distribution of the organic matter.

No. 28046—Opaline Cherty Shale:

This rock is of the same geological age as No. 19374 and No. 28045 and strongly resembles them. The following differences, however, are noteworthy: In No. 28046 the detrital quartz and feldspar content is lower, and these grains are smaller; spherules of chalcedony are fairly abundant in the groundmass; glauconite and organic matter are more plentiful than in No. 28045 and occur in concentrated form parallel with the laminæ; although the groundmass is composed chiefly of opaline silica, it nevertheless appears partly pleochroic under high power and indicates the presence of intermixed diagenetic minerals (formed after deposition). No free dolomite or calcite was observed in this material, and what lime content is found on chemical analysis will be due in large part to the fossils and the

detrital plagioclase grains. Due to concentration of organic matter and clay in definite layers, this rock is more laminated than No. 28045, and the evident lack of opaline replacement along these laminae suggests the easy cleavability of this material.

No. 30704—(Dark) Opaline Chert:

Dark brown stringy accumulations of organic matter parallel the bedding, which is frequently distorted. An occasional quartz or orthoclase fragment is enclosed by opaline groundmass. Sample carries a few channels of brecciated material, cemented by opaline veinlets and clay. The quartz and orthoclase are the only recognizable anisotropic minerals observed in this material. Matrix predominantly opaline silica with some undistinguishable clay minerals. Material shows no evidence of chalcidonic replacements, and no fossils.

APPENDIX II

SAND IDENTIFICATION

Group I.—In this group rock fragments consist chiefly of granitic rock and sandstone with less than 15% quartzite, rhyolite, andesite, siltstone, and limestone, and from 4% to 15% shale and chert. The mineral grains consist chiefly of quartz and feldspar, with less than 10% of pyroxene, amphibole, mica, magnetite, hematite, limonite, serpentine, and calcite. Sands Nos. 1 to 6 in this group were secured from the following places:

Sand No.	Source
1	Santa Clara River at Saticoy, Ventura County
2	Sisquoc River at Sisquoc, Santa Barbara County
3	Piru Creek at Santa Clara River, Ventura County
4	Oro Fino, tributary to Salinas River, Monterey County
5	Bank adjacent to Salinas River at Atascadero, San Luis Obispo County
6	Salinas River at Templeton, San Luis Obispo County.

Group II.—Rock fragments in Group II consist chiefly of granitic rock and gneiss in Southern California, and of graywacke (sandstone) in Northern California, with less than 10% of basalt, andesite, quartzite, and jasper and usually less than 1% of shale and chert. Mineral grains in Group II are similar to Group I. Sands Nos. 20 to 24 in this group were found in:

Sand No.	Source
20	Coyote Creek, Santa Clara County
21	Russian River, Healdsburg, Sonoma County
22	Livermore Valley, Alameda County
23	Near Olympia, Santa Cruz County
24	Roscoe, San Fernando Valley, Los Angeles County
25	Irwindale, San Gabriel Valley, Los Angeles County
26	Monrovia, San Gabriel Valley, Los Angeles County
27	San Joaquin River at Friant, Fresno County

Group III.—The sands in Group III were made by crushing ledge rock to the desired gradation. Sands Nos. 101 and 102 in this group were found in:

Sand No.	Source
101	Crushed hornblende diorite, Logan, San Benito County
102	Crushed quartz, Jackson, Calaveras County.

APPENDIX III

CEMENT CLASSIFICATION

The cements used in the investigation were analyzed as shown in Table 5.

TABLE 5.—CEMENT ANALYSES

Cement identi- fication	OXIDE ANALYSIS (PERCENTAGES)							COMPOUND COMPOSITION (PERCENTAGES)				MERRIMAN ALKALI TEST		Auto- clave test (per- centage experi- ment)
	Si O ₂	Fe ₂ O ₃	Al ₂ O ₃	Ca O	Mg O	SO ₃	Alkali as Na ₂ O	C ₄ AF	C ₃ A	C ₂ S	C ₃ S	Alka- linity	Free alkali	
AS	22.76	2.00	4.02	66.04	1.80	1.54	0.45	6.1	7.2	62.3	17.9	3.3	1.0	0.05
BL	23.76	2.48	4.34	64.58	1.61	1.61	0.51	7.6	7.2	41.1	37.2	4.1	4.1	0.12
CL	20.42	5.68	5.92	62.86	1.57	1.74	0.77	17.3	5.8	52.5	17.6	3.6	2.5	0.09
DL	22.26	3.60	4.73	63.18	2.93	1.38	0.90	10.9	6.4	48.5	26.8	4.1	5.1	0.21
EL	21.57	3.52	4.49	62.44	4.08	1.50	0.92	10.6	6.1	50.8	23.3	3.8	3.7	0.25
FS	21.00	3.12	5.39	64.80	1.84	1.51	0.92	9.4	9.0	61.0	13.5	3.8	3.6	0.10
FL	23.34	3.96	4.28	64.32	1.09	0.87	0.50	12.1	4.6	49.5	28.8	3.5	2.6	0.05
FA	25.35	3.87	3.42	63.52	1.62	1.22	0.56	11.8	2.6	34.6	46.2	3.6	2.0	0.01
GS	21.48	2.72	5.64	64.50	1.72	1.71	1.14	8.2	10.3	54.1	20.3	5.1	6.3	0.09
GL	20.02	5.35	5.49	62.80	1.65	1.81	1.10	16.4	5.6	58.2	12.0	5.0	6.2	0.05
HS	21.14	2.48	6.43	64.16	2.23	1.78	0.69	7.5	12.8	49.5	23.0	3.3	1.5	0.18
HL	21.59	4.80	5.17	62.61	1.72	1.89	0.53	14.6	5.6	45.2	27.3	3.5	1.4	0.05
HP	31.10	2.40	6.77	53.30	1.86	1.57	0.78	Portland puzzolanic type				...	...	0.01
IS	22.56	2.40	5.52	65.33	1.48	1.49	0.44	7.3	10.6	50.1	26.7	3.2	2.1	0.17
M	21.30	2.90	5.70	63.44	2.78	1.97	0.83	8.8	10.3	49.4	23.4	4.2	4.4	0.12
N	22.34	3.78	4.78	63.32	3.44	1.51	0.47	11.5	6.3	46.1	29.3	3.1	1.6	0.10
O	21.65	3.55	5.65	63.35	1.45	1.85	0.51	10.8	9.0	46.0	27.0	3.7	3.9	0.01
R	22.37	4.00	4.35	64.65	1.36	1.45	0.64	12.2	4.8	54.5	22.8	3.8	2.7	0.01

In the identifying letters given in the first column, the first letter refers to the brand and the second letter to the type of cement, as follows:

S = Standard cement; in some cases the standard product contains less than 8% of C₃A and therefore might also be classified as a low or moderately low C₃A cement.

L = Cement having less than 8% C₃A and complying with American Association of State Highway Officials Specification M-60-38 as distinguished from the standard product of the same manufacturer with higher C₃A content.

A = Low-heat type "A."

P = Portland-puzzolan; insoluble, 15.44; all other cements less than 0.85% insoluble; cements *M*, *N*, *O*, and *R* are from mills outside California.

A TRIBUTE TO **“Calculation of the Compounds in Portland Cement”**

by R.H. Bogue

Foreword by Paul Brown

Portland cements are primarily composed of compounds containing CaO , SiO_2 , Al_2O_3 , and Fe_2O_3 . It is well recognized that the compounds formed from these oxides during cement production determine concrete properties. Bogue’s publication is seminal in permitting the determination of the actual compounds present in a portland cement based on an oxide analysis.

Bogue’s analyses relied on his appreciation of the results of prior studies and theoretical analyses that had been carried out during the 50 or so years prior to his publication. Various studies were initiated in the latter half of the 19th century to establish the nature of the compounds present in cements. Significant among these, in the 1880s, LeChatelier identified $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot 2(\text{Fe}, \text{Al})_2\text{O}_3$ in clinker phases by microscopical means. Also relying on optical microscopy, Tornebohm identified the major cementing phases and named them alite, belite, celite, and felite about the turn of the 20th century. These developments specific to clinker chemistry were accompanied by theoretical advances and development of new experimental techniques. Two events are notable with regard to characterization of cements. In 1878, Gibbs enunciated the phase rule and by doing so provided the basis for understanding aspects fundamental to heterogeneous equilibria between solids and liquids whose compositions may differ from each other. This provided the basis for understanding the events that occur when multicomponent oxide melts are crystallized. In 1913 and 1914, the Braggs established the technique of X-ray diffraction as a means to characterize crystalline solids. This permitted the determination of the crystalline solids present in cements as well as allowing an estimate of their proportions.

When the polished section of a polycrystalline, polyphase solid is viewed by microscopy, certain conclusions regarding the compositions of the solids present and their crystallization paths can be reached. Systematic variations in bulk composition can be used to establish the stability ranges for various compounds that may be present. If the compounds are minerals or synthetic analogs, indices of refraction can be used to estimate compositions. With regard to spatial distributions,

46 Bogue

compounds that crystallize first tend to be surrounded by those that crystallize at lower temperatures. For cement clinker, those phases that crystallize at lower temperatures are commonly called interstitial compounds. It is these phases that form a liquid at clinkering temperatures and it is from them that alite and belite form. Finally, rapid cooling can be used to quench in and observe compounds or polymorphs, such as $3\text{CaO} \cdot \text{SiO}_2$, that would otherwise decompose with slow cooling. Grinding clinker to powder and carrying out X-ray diffraction allows detailed compositional analyses and permits effects of solid solution behavior to be assessed.

Bogue generalized these observations and reached the following conclusions:

- (1) Only five oxides are present in clinker and these are CaO , SiO_2 , Al_2O_3 , Fe_2O_3 , and MgO .
- (2) All of the Fe_2O_3 present participates in the formation of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$.
- (3) MgO does not form any compounds and remains uncombined.
- (4) Any Al_2O_3 that does not react to form $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ reacts to form $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.
- (5) Any CaO that is not consumed in the above reaction combines to form $2\text{CaO} \cdot \text{SiO}_2$.
- (6) Any CaO not used in the formation of $2\text{CaO} \cdot \text{SiO}_2$, then reacts with it to form $3\text{CaO} \cdot \text{SiO}_2$.
- (7) Any CaO that remains after the $2\text{CaO} \cdot \text{SiO}_2$ has reacted completely stays uncombined as free lime.

These observations were quantified by Bogue to calculate the proportions of cementing compounds as follows:

Deduct the proportion of free lime.

$$C_4\text{AF} = 3.0\text{Fe}_2\text{O}_3.$$

$$C_3\text{A} = 2.7\text{Al}_2\text{O}_3 - 1.7\text{Fe}_2\text{O}_3.$$

$$C_2\text{S} = 8.6\text{SiO}_2 + 1.1\text{Fe}_2\text{O}_3 + 5.1\text{Al}_2\text{O}_3 - 3.1\text{CaO}$$

$$C_3\text{S} = 4.1\text{CaO} - 7.6\text{SiO}_2 - 1.4\text{Fe}_2\text{O}_3 - 6.7\text{Al}_2\text{O}_3$$

When applied to cement, rather than clinker, the proportion of CaO is reduced by 0.7SO_3 to account for the presence of calcium sulfate.

Bogue understood both cement chemistry and kiln chemistry well enough to appreciate the fact that the sequence of crystallization is actually the inverse of the sequence with which the aforementioned equations are solved in the calculation of the compounds present. In particular, the silicates form at a temperature where the aluminate and ferrite compounds are in the liquid state. The reaction between CaO and SiO_2 can locally produce C_2S , C_2S , and C_3S or C_3S only, depending on the local equilibria. Subsequently, the aluminate phase crystallizes and finally the ferrite phase. As Bogue points out in his book on cement chemistry [1], various subsequent refinements of the calculation of the phase proportions were carried out. It is now well understood that the Bogue calculation gives incorrect results. In particular, the Bogue calculation tends to underestimate the proportion of alite while overestimating that of belite. It is for this reason that the Bogue calculation of commonly cited as determining the “potential” phase composition of portland cement. There are two reasons for this. The first is that equilibria might not have been reached during clinker cooling. The second and more important reason is that the compositions of the major cement compounds depart from the ideal compositions [2]. Consequently, aluminum and iron oxide are present in the silicate phases and silica substitution occurs in the interstitial phases. Additionally, substitutions of alkalis, titania, magnesia, phosphate, and

sulfate also occur. Because the Bogue calculation involves the solution of four linear equations with four unknowns, it can be optimized by making various assumptions regarding the compositions of the phases that are produced as regards these substitutions. Regardless of these substitutions, however, the Bogue calculation, which assumes cementing compounds to be C_3S , C_2S , C_3A , and C_4AF , is still widely relied on. Both the importance and the general acceptance of Bogue's calculation scheme are demonstrated by its inclusion in ASTM C150, "Standard Specification for Portland Cements." [3]

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Calculation of the Compounds in Portland Cement¹

R. H. Bogue

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SYSTEMS containing combinations of the components CaO , MgO , Al_2O_3 , Fe_2O_3 , and SiO_2 have been studied and reported by this and other laboratories (3, 5, 7, 8, 10, 11). It has been found that when these components are intimately mixed in proportions similar to those found in Portland cements, and burned to equilibrium, the following compounds are formed: $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{SiO}_2$, and MgO .

Note—In a former publication (5) it was reported that MgO enters into solid solution with $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, the end member of the series being $4\text{CaO} \cdot 2\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. Magnesia in excess of that required for the above combination was found to remain as uncombined MgO . More recent information obtained in this laboratory indicates that the amount of the solid solution is much smaller than had previously been reported. Although there is no reasonable doubt that a large part of the magnesia remains uncombined, the exact nature and degree of the reaction by which the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ is changed in color and pleochroism in the presence of a small amount of magnesia has not been determined. This problem is under further investigation. At present the magnesia may be considered as remaining essentially uncombined, and the iron compound as existing essentially in the form of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$.

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The bases for a calculation of the compounds present in Portland cement from chemical analyses are presented. Arithmetical and diagrammatical methods are given for such a calculation. The compounds considered are $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, uncombined MgO , uncombined CaO , and CaSO_4 . Other components than those included in these compounds are not at present considered as their forms of combination are not known.

In addition to the five components listed above, commercial Portland cements contain small amounts of other materials in variable quantity. These may include soda, potash, titania, manganese oxides, phosphates, and perhaps still other materials.

The total amount of these

lesser components, however, probably does not often exceed 2 per cent.

The manner of combination of these lesser components is not known. It is possible that some of them, as perhaps the alkalis, may have a significant influence on the relative amounts of the major compounds that are formed, but since the manner of their combination is not yet known, the effects of their presence cannot now be evaluated. Consequently, it is not possible at present to consider those components in the calculation of cement constitution.

It is assumed that the compounds of Portland cement are essentially the same as those of the pure five-component system given above when the components are present in the proportions found in commercial cements. The general correctness of this assumption has been confirmed by information obtained from cooling curves (4), from microscopic examinations (1) and from x-ray diffraction photographs (1).

Manner of Reaction

The manner in which the components react determines the relative amounts of the resulting compounds. Information obtained at this laboratory leads to the following generalizations:

- (1) The ferric oxide reacts with alumina and lime to form $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. (See note.)
- (2) The magnesia remains essentially in the form of uncombined MgO .
- (3) The alumina remaining from combination as $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ reacts with lime to form $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.
- (4) The lime remaining from the above combinations reacts with the silica. The compound $2\text{CaO} \cdot \text{SiO}_2$ is formed, and any CaO then uncombined reacts with the $2\text{CaO} \cdot \text{SiO}_2$ to form $3\text{CaO} \cdot \text{SiO}_2$. If CaO remains after converting all of the $2\text{CaO} \cdot \text{SiO}_2$ to $3\text{CaO} \cdot \text{SiO}_2$, it will be present as uncombined CaO .

The formation of the compounds as described assumes that a condition of equilibrium has been reached during the progress of the reactions in the kiln. A small amount of uncombined CaO may remain in the clinker, however, indicating (if the composition is such that the CaO would be completely combined at equilibrium) that the reactions are not altogether complete. This departure from complete combination is not usually of sufficient magnitude to produce a change in the nature of the compounds formed, but it does produce a change in the relative amounts of the compounds produced. For that reason it is important that free CaO in the cement be determined (9) and that the amount present be taken into consideration in the calculation of the constitution. If this is not done, an error of usually small but uncertain magnitude may be introduced.

The "insoluble residuc" obtained in a cement analysis is composed of quartz, titania, and several other materials. The amount of the residue is usually very small, about 0.2 per cent. Because of the low quantity of this material and the variable and uncertain nature of its composition, it seems inexpedient to attempt to introduce a correction factor for it. In unusual cases where the amount of the residue is high, it may be desirable to analyze it to ascertain if an appreciable quantity of silica has remained as free quartz. If the residue is found to contain an appreciable amount of silica, then the silica content of the residue should be deducted from the total SiO_2 to obtain the value of the SiO_2 taking part in the reactions.

The "ignition loss" consists essentially of moisture and carbon dioxide that have been taken up by the cement following the burning operation. In calculating the constitution, this value is accordingly set down without further change.

By means of the information given above, the relative amounts of the compounds present in Portland cement or clinker may be calculated from the chemical analyses. It is essential in any case to consider the SO_3 content and calculate that to CaSO_4 .

Accuracy of Computations

The accuracy of the computations depends on the correctness of both the postulations and the analytical values. The postulations as given represent the best available information, but are subject to revision and extension as has been pointed out. The general correctness of the analytical values will vary with the conditions of test and the personal factor. In any case it is not recommended that analyses be considered as accurate beyond the first decimal place.

An examination of the factors given below will show that errors of analysis often are magnified in the computations for compound composition. Thus a plus error (other values remaining fixed) of 0.2 per cent CaO or uncombined CaO (expressed as percentage of the cement) will increase the computed $3\text{CaO} \cdot \text{SiO}_2$ about 0.8 per cent and decrease the com-

puted $2\text{CaO} \cdot \text{SiO}_2$ about 0.6 per cent. A plus error of 0.2 per cent Fe_2O_3 will increase the computed $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ about 0.6 per cent, decrease the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ about 0.3 per cent, decrease the $3\text{CaO} \cdot \text{SiO}_2$ about 0.3 per cent, and increase the $2\text{CaO} \cdot \text{SiO}_2$ about 0.2 per cent. A plus error of 0.2 per cent Al_2O_3 will increase the computed $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ about 0.5 per cent, decrease the $3\text{CaO} \cdot \text{SiO}_2$ about 1.3 per cent, and increase the $2\text{CaO} \cdot \text{SiO}_2$ about 1.0 per cent. A plus error of 0.2 per cent SiO_2 will decrease the computed $3\text{CaO} \cdot \text{SiO}_2$ about 1.5 per cent and increase the $2\text{CaO} \cdot \text{SiO}_2$ 1.3 per cent. For these reasons only analytical data that are believed to be reliable should be employed for the computation of compound composition, and an expression of the compounds $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot \text{SiO}_2$, and $2\text{CaO} \cdot \text{SiO}_2$ should not be given to a closer approximation than the nearest whole number.

Method of Calculation

Each per cent of SO_3 enters into combination with 0.70 per cent CaO to form 1.70 per cent CaSO_4 :

$$\frac{\text{CaO}}{\text{SO}_3} = \frac{56.07}{80.065} = 0.70 \text{ per cent CaO} \dots\dots\dots (c_1)$$

Each per cent of Fe_2O_3 enters into combination with 0.64 per cent Al_2O_3 :

$$\frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3} = \frac{101.92}{159.68} = 0.64 \text{ per cent Al}_2\text{O}_3 \dots\dots\dots (a_1)$$

and with 1.40 per cent CaO :

$$\frac{4\text{CaO}}{\text{Fe}_2\text{O}_3} = \frac{224.28}{159.68} = 1.40 \text{ per cent CaO} \dots\dots\dots (c_2)$$

to form 3.04 per cent $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$.

The total MgO is recorded as uncombined MgO .

The total Al_2O_3 minus (a_1) gives the Al_2O_3 (a_2) available for combination as $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Each per cent of (a_2) will enter into combination with 1.65 per cent CaO to form 2.65 per cent $3\text{CaO} \cdot \text{Al}_2\text{O}_3$:

$$\frac{3\text{CaO}}{\text{Al}_2\text{O}_3} = \frac{168.21}{101.92} = 1.65 \text{ per cent CaO} \dots\dots\dots (c_3)$$

The amount of CaO available for combination with SiO_2 is obtained by subtracting from the total CaO the sum of the uncombined CaO , the CaO (c_1) combined as CaSO_4 , the CaO (c_2) combined as $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, and the CaO (c_3) combined as $3\text{CaO} \cdot \text{Al}_2\text{O}_3$:

$$\text{Total CaO} - (\text{uncombined CaO} + c_1 + c_2 + c_3) = \text{CaO available to combine with SiO}_2 \dots\dots (c)$$

The total SiO_2 (s) , unless corrected for silica in the "insoluble residue," is calculated first to combine with CaO to form $2\text{CaO} \cdot \text{SiO}_2$. Each per cent of SiO_2 (s) will combine with CaO to form 2.87 per cent $2\text{CaO} \cdot \text{SiO}_2$:

$$\frac{2\text{CaO} \cdot \text{SiO}_2}{\text{SiO}_2} = \frac{172.20}{60.06} = 2.87 \text{ per cent } 2\text{CaO} \cdot \text{SiO}_2$$

This first approximation to the value of $2\text{CaO} \cdot \text{SiO}_2$ is subtracted from the SiO_2 $(s) + \text{CaO}$ (c) , which gives the CaO (c_4) available to combine with $2\text{CaO} \cdot \text{SiO}_2$ to form $3\text{CaO} \cdot \text{SiO}_2$.

Each per cent of CaO (c_4) combines with $2\text{CaO} \cdot \text{SiO}_2$ to form 4.07 per cent $3\text{CaO} \cdot \text{SiO}_2$:

$$\frac{3\text{CaO} \cdot \text{SiO}_2}{\text{CaO}} = \frac{228.27}{56.07} = 4.07 \text{ per cent } 3\text{CaO} \cdot \text{SiO}_2$$

The $3\text{CaO} \cdot \text{SiO}_2$ subtracted from the total SiO_2 $(s) + \text{CaO}$ (c) gives the true amount of $2\text{CaO} \cdot \text{SiO}_2$ present.

If the computed $3\text{CaO} \cdot \text{SiO}_2$ is greater than $s + c$, no $2\text{CaO} \cdot \text{SiO}_2$ is present. In that case each per cent of SiO_2 (s) combines with CaO to form 3.80 per cent $3\text{CaO} \cdot \text{SiO}_2$:

$$\frac{3\text{CaO} \cdot \text{SiO}_2}{\text{SiO}_2} = \frac{228.27}{60.06} = 3.80 \text{ per cent } 3\text{CaO} \cdot \text{SiO}_2$$

This amount of $3\text{CaO} \cdot \text{SiO}_2$ subtracted from SiO_2 $(s) + \text{CaO}$ (c) gives the percentage of uncombined CaO . The above

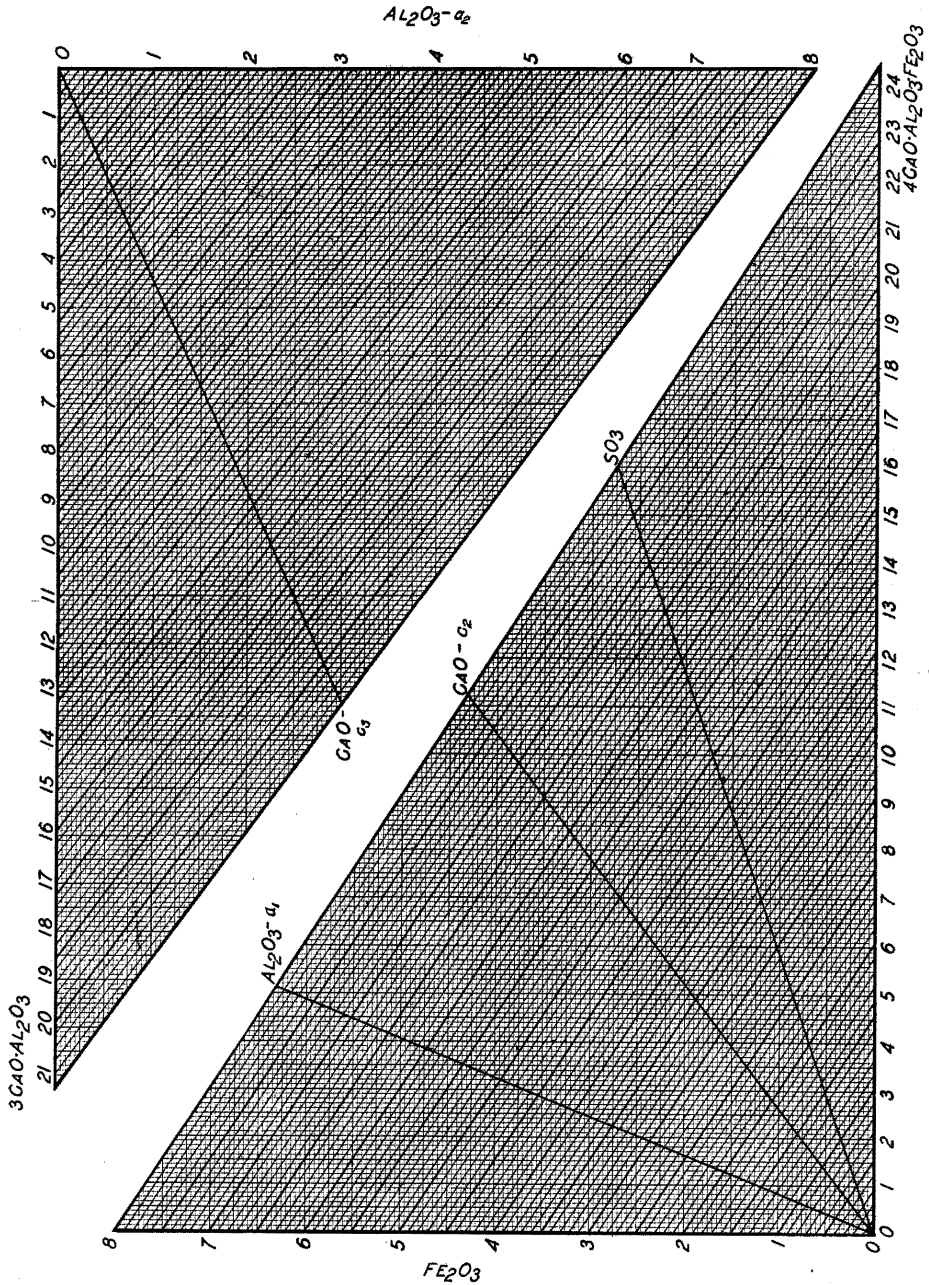


Figure 1

condition can obtain only when the lime is in excess of that which can go into combination at equilibrium, and the uncombined CaO has not been determined and deducted as previously described.

Application of the Method

A diagrammatic method for obtaining these relations has been found useful in computing the amounts of the compounds from chemical analyses. Such a method has not the precision

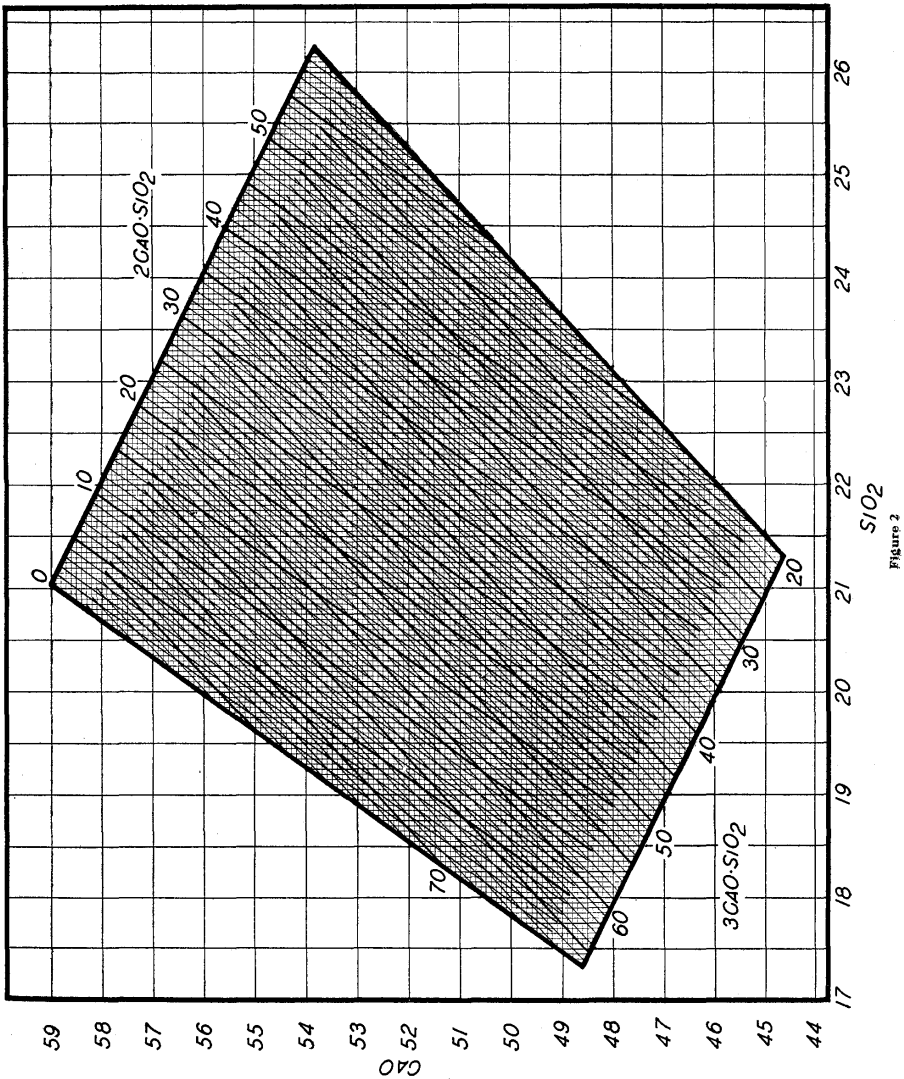


Figure 2

of the mathematical factors, but the values read are probably within the accuracy of the analytical procedures and the method has the advantage of speed and simplicity.

In Figures 1 and 2 the relations expressed in the factors given above are plotted in a convenient form. As an illustration of the use of the diagrams and the factors, an analysis of a commercial cement and the computation of compounds are presented. A chart (Table I) will be found an aid in the proper recording of the significant figures. The analytical data are given on the chart, together with the values as read from the diagrams. A few abbreviations appear on the chart:

C_4AF for $4CaO.Al_2O_3.Fe_2O_3$, C_3A for $3CaO.Al_2O_3$, C_2S for $3CaO.SiO_2$, and C_2S for $2CaO.SiO_2$.

The values for ignition loss, 1.1, and magnesia, 3.7, are transferred to the lower horizontal row, wherein are placed the compounds of the cement.

The value for free CaO , 0.3, is transferred to the "free CaO " column opposite CaO , and brought down to the lower row compounds.

The value for SO_3 , 2.0, is transferred to the " SO_3 eq." column, and the CaO equivalent read from the lower diagram in Figure 1.

In this case only, both readings are taken from the horizontal axis. It is desired to find the CaO equivalent of 2.0 SO_2 in the formation of CaSO_4 . The point 2.0 on the horizontal axis of the lower diagram in Figure 1 is followed upward on the vertical coordinate until it intercepts the radial line for SO_2 . The diagonal coordinate is then followed until the radial line for CaO is intercepted. The vertical coordinate is again followed down from that point to the horizontal axis, and the value 1.4 obtained.

The value read, 1.4, is placed at c_1 and the sum of the two, 3.4, is placed at the bottom of the column under " CaSO_4 ."

The value for Fe_2O_3 , 3.4, is transferred to the " Fe_2O_3 eq." column and the Al_2O_3 and CaO equivalent to the Fe_2O_3 read from the lower diagram in Figure 1.

It is desired in this case to find the Al_2O_3 and CaO equivalents of 3.4 Fe_2O_3 in the formation of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. The point 3.4 on the vertical axis of the lower diagram in Figure 1 is followed on the diagonal coordinate until it intercepts the radial line for Al_2O_3 . The vertical coordinate is then followed down from that point and the value 2.2 Al_2O_3 read off on the horizontal axis. The point 3.4 on the vertical axis is again followed on the diagonal coordinate until it intercepts the radial line for CaO. Again the vertical coordinate is followed downward and the value 4.8 CaO read off on the horizontal axis.

The values as read are placed in the column at their proper places: the Al_2O_3 , 2.2, at a_1 ; and the CaO, 4.8, at c_2 . The three figures in the column are now added to give the $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. This value to the nearest whole number is placed at the base of the column. The amount also may be read directly from the diagram if desired.

Table I—Chart Used for Recording Significant Data in Computation of Compounds

COMPONENTS	ANALYSIS	FREE CaO	SO_2 Eq.	Fe_2O_3 Eq.	Al_2O_3 Eq.	c AND s	C ₅ S
CaO	62.8	0.3	a_1 1.4	c_2 4.8	c_1 3.8	c 52.5	
MgO	3.7			a_2 2.2	a_1 2.3		
Al_2O_3	4.5			3.4		s 22.3	
Fe_2O_3	3.4						
SiO_2	22.3		2.0				
SO_2	2.0						
Loss	1.1						
Insoluble Free CaO	0.1						
	0.3						
Ignition loss	Free MgO	Free CaO	CaSO_4	C_2AF	C_3A	C_3S	C_5S
1.1	3.7	0.3	3.4	10	6	44	31

The value a_1 , 2.2, is subtracted from Al_2O_3 , 4.5, to give a_2 , 2.3, the Al_2O_3 available to combine as $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, which is placed in the " Al_2O_3 eq." column at a_2 . The CaO equivalent of this, 3.8, is read from the upper diagram of Figure 1 and placed at c_1 . The two values are added to give the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and that figure to the nearest whole number brought to the foot of the column. This value also may be read directly if desired.

The CaO, c, available for combination with the silica is now found by subtracting from the total CaO the free CaO, c_1 , c_2 , and c_3 : $62.8 - (0.3 + 1.4 + 4.8 + 3.8) = 52.5$ which is set down at c. The total SiO_2 , 22.3 (unless corrected for the quartz in the insoluble residue) is set down at s.

The computed tricalcium silicate and dicalcium silicate are now read directly from the diagram (2) in Figure 2. The point is found which is the intersection of the vertical coordinate representing SiO_2 (s) and the horizontal coordinate representing the CaO (c) available for combination with the silica. The $3\text{CaO} \cdot \text{SiO}_2$ corresponding to this point, 44 per cent, is read to the nearest whole number on the diagonal coordinate that is parallel to the lower right base line, as indicated. The $2\text{CaO} \cdot \text{SiO}_2$, 31 per cent, is read on the diagonal coordinate that is parallel to the upper left base line, as indicated. These values are set down in the lower row of compounds under C_3S and C_2S , respectively.

In the event that the point represented by the intersection of the coordinates for CaO and SiO_2 lies to the left of the diagram, there is present an excess of lime above that required

to convert all of the $2\text{CaO} \cdot \text{SiO}_2$ to $3\text{CaO} \cdot \text{SiO}_2$. In that case there is some uncombined CaO present and no dicalcium silicate. The tricalcium silicate content is found by reading that value at the point where the SiO_2 coordinate intersects the upper left boundary of the figure. The lime required for that compound is then read off on the CaO (horizontal) coordinate and the remaining lime is uncombined. For example, consider that $c = 59.0$ and $s = 20.5$. The SiO_2 coordinate cuts the upper boundary at a point represented by about 78 per cent $3\text{CaO} \cdot \text{SiO}_2$. The CaO required is read to be 57.5 per cent. The free CaO is then 1.5 per cent. Such a value should be recorded in the "free CaO" column opposite SiO_2 and brought to the lower row of compounds.

The upper right boundary curve as drawn represents the compositions at which the sum of the two calcium silicates is 80 per cent. The remaining material includes all other compounds—as $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, MgO, alkalis, free CaO if present, CaSO_4 , and any other constituents. The lower left boundary curve as drawn represents the compositions at which the sum of the two silicates is 65 per cent, the remaining 35 per cent being the other compounds as above. It is probable that most commercial cements fall within these limits, but the diagram may be extended up to the line representing 100 per cent $2\text{CaO} \cdot \text{SiO}_2$ plus $3\text{CaO} \cdot \text{SiO}_2$, and down as far as desired. The upper left boundary is the line for zero $2\text{CaO} \cdot \text{SiO}_2$ and the lower right boundary is cut at 20 per cent $3\text{CaO} \cdot \text{SiO}_2$ since Portland cements will scarcely be found with less than that amount of the tribasic silicate. If desired, however, the diagram may be extended to the lower right to zero $3\text{CaO} \cdot \text{SiO}_2$.

The data necessary to construct the diagrams in Figure 1 are obtainable from the factors previously given. The following locations of the external angles of the diagram in Figure 2 will define the position of that figure.

	LEFT	TOP	RIGHT	BOTTOM
CaO	48.64	58.95	53.81	44.70
SiO_2	17.36	21.05	26.19	21.30

The diagrams must be prepared with the highest precision and should be drawn to such a scale that estimates may properly be made to 1 per cent.

There now appear on the bottom row of the chart the values for all of the compounds which we are able at present to calculate from the chemical analysis of a cement.

The use of factors in the calculation gives values differing but slightly from those obtained by the use of the diagrams. This is brought out in Table II, in which are shown the values obtained by factors and by the diagrams from the composition represented by the analysis given. In this case, in order to demonstrate the difference, the values are expressed to the first decimal place.

Table II—Comparison of Computations by Factors and by Diagram

COMPONENTS	ANALYSIS	COMPOUNDS	
		BY FACTORS	BY DIAGRAM
	Per cent	Per cent	Per cent
CaO	62.8	$2\text{CaO} \cdot \text{SiO}_2$	44.4
MgO	3.7	$2\text{CaO} \cdot \text{SiO}_2$	30.5
Al_2O_3	4.5	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	6.1
Fe_2O_3	3.4	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	10.3
SiO_2	22.3	Free MgO	3.7
SO_2	2.0	Free CaO	0.3
Ignition loss	1.1	CaSO_4	3.4
Insoluble ^a	0.1	Ignition loss	1.1
Free CaO ^a	0.3		1.1
Total	99.8		99.8

^a Not included in total.

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A TRIBUTE TO
**“Expression and Analysis of Pore
Fluids from Hardened Cement
Pastes and Mortars”**

by R.S. Barneyback Jr. and S. Diamond

Foreword by Kevin J. Folliard

The definition of a landmark paper can not be found in a dictionary, encyclopedia, or Wikipedia, for that matter. But a paper that advances the state of the art, builds upon previous research accomplishments, is cited in many subsequent publications, and whose key products or techniques are used by researchers for decades certainly would satisfy the definition of landmark. Such is the case for the following paper by Barneyback and Diamond (1981), whose research described in the paper built upon the pioneering work of Longuet et al. (1973) and led to the development of an improved apparatus for expressing pore solution from hardened pastes or mortars. The apparatus and techniques described by Barneyback and Diamond have since been used by a variety of researchers to extract and analyze pore solution for studies on topics ranging from cement hydration to alkali-silica reaction to corrosion of reinforcing steel. As a testament to the effect of this paper on researchers and practitioners, well over 100 technical papers have cited this specific paper. This foreword briefly describes some key aspects of this paper and discusses its effect since its publication in 1981.

This paper describes the development of an apparatus for expressing pore solution from hardened paste or mortar and describes appropriate methods for analyzing the expressed pore solution. As highlighted by the authors, the apparatus, referred to in the paper as a “pore fluid expression device” and typically referred to today simply as a “pore press,” was designed and constructed based on previous work by Longuet et al. (1973), but with significant modifications and improvements to allow it to be used for testing mortars (and concretes), as opposed to just cement pastes. The device described by Barneyback and Diamond was able to operate at pressures up to 550 MPa (80,000 psi), as opposed to the device developed by Longuet et al, which was only able to operate at pressures up to 350 MPa (~ 50,000 psi). The device described by Barneyback and Diamond and

56 Barneyback Jr. and Diamond

illustrated in Figure 1 of their paper was used extensively at Purdue University in the years leading to the publication of this landmark paper and was a key tool used by Barneyback in his highly-regarded PhD research on alkali-silica reaction (1981).

The design and construction of a device to safely extract pore solution from hardened pastes, mortars, and concretes is by no means trivial. As described in the paper, the device is constructed using heat-treated alloys and the fabrication method employs a shrink fitting technique that allows the outer cylinder to be tightly bonded to the inner cylinder, essentially precompressing the inner cylinder. As the authors vividly point out, this design, coupled with other key design and construction features, prevents catastrophic failure of the device, which could otherwise be a major safety concern. In addition to the innovative design of the body of the apparatus, the authors incorporated other key innovations into the device to allow the pore solution to be drawn from the specimen under load, down through a drain ring and channel, and out through a tube to an awaiting syringe. The authors provide important details in the paper on what type specimens should be tested in the apparatus and how the load should be applied (and removed) to extract the desired volume of pore solution. Lastly, the authors describe how the extracted pore solution should be analyzed to determine the types and amounts of dissolved ions.

This paper focuses primarily on the pore solution extraction device, including its design, construction, and use, and also provides key information on how to accurately measure the composition of the pore solution. It is a well-written, detailed paper that has been read and cited by many, and most importantly, the apparatus described in the paper (or similar types of devices) has been used extensively.

So one question that may come to mind is – Why would one want to know the composition of pore solution in portland cement-based systems? As Barneyback and Diamond clearly point out, the hydration of portland cement takes place through direct interactions with pore solution, with hydration before setting occurring between cement compounds and a continuous liquid phase, and hydration after setting occurring between cement compounds and a discontinuous pore solution. The authors note the relative ease of extracting pore solution from fresh pastes (or mortars or concretes), as the pore solution can easily be extracted by filtration (with or without a vacuum). The real challenge is extracting the pore solution from a hardened matrix, which is the challenge that is overcome with the pore press developed by Barneyback and Diamond. With this apparatus, researchers can and have evaluated pore solution in mature concrete and related its composition to several key aspects of concrete behavior, especially with regard to durability issues. A few examples are provided next for conciseness as a more exhaustive review of work based on pore solution extraction and analysis is beyond the scope of this foreword.

Alkali-silica reaction (ASR) is a common form of concrete distress and one that is much better understood today because of mechanistic studies that have employed pore solution extraction and analysis techniques. Various studies on ASR have evaluated pore solution composition to gain insight into the role of supplementary cementing materials (Shehata et al., 1999; Thomas and Shehata, 2004) and lithium compounds (Diamond, 1999; Diamond and Ong, 1992; Bérubé et al., 2004) in

suppressing ASR, and the potential release of alkalis from aggregates (Constantiner and Diamond, 2003). Research on corrosion of reinforcement steel, another phenomena greatly affected by pore solution composition, has also benefited from research performed using pore solution extraction and analysis. The pioneering work of Page and Vennesland (1983) showed the strong effect of silica fume in reducing both pore solution alkalinity and chloride-binding capacity, which has direct relevance to the corrosion process.

In summary, this landmark paper by Barneyback and Diamond has had a significant effect on cement and concrete research over the past 25 years or so. A number of researchers have since used the pore solution extraction and analysis techniques described in this paper for studies focusing on topics ranging from cement hydration to alkali-silica reaction to corrosion of reinforcing steel. It is likely that researchers will continue using these techniques in the future to further advance our understanding of portland cement concrete.

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58 Barneyback Jr. and Diamond

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