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**Research Report 18-C**

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***The Alkali-Aggregate  
Reaction in Concrete***

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**HIGHWAY RESEARCH BOARD**

**Research Report 18-C**

***The Alkali-Aggregate  
Reaction in Concrete***

A resume of Field Experience, Laboratory Tests for Reactivity of Aggregates, and a Review of the Fundamental Research to show the mechanism of the reaction.

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## *Foreword*

In 1940 T. E. Stanton first reported that the cause of deterioration of certain concretes in California was an expansive reaction between the alkalis in the cement and certain constituents of the aggregate. Since that time, there have been many reports relating to this problem. These reports, ranging from summaries of field experiences to carefully controlled laboratory studies of the basic fundamentals involved, collectively reflect the complexity of the problem. Often, the data presented and the conclusions drawn by various investigators appear to contradict each other. As a result, it is difficult to establish specific relations that are true in all instances.

The Highway Research Board Committee on Durability of Concrete—Chemical Aspects for a period of several years has directed its attention to a study of the alkali aggregate problem. At the 1957 Annual Meeting of the Board, a general discussion of this problem was sponsored by this committee. The planned discussion was centered around three major parts: One dealt with field experiences; a second with the laboratory tests that have been devised to detect potentially reactive aggregates; and the third was concerned with theoretical considerations and present research. This report generally presents the information obtained in that session, as well as some additional information made available to the committee.

These reports and discussions do not cover all phases of the problem. The committee has made no attempt to evaluate the data or discussions presented, as it is felt that the complete reporting of the individual viewpoints will be of the greatest value to those interested in the problem.

In addition to the written discussions included in this report, a number of persons took part in the verbal discussions during the session and the committee wishes to thank them for adding greatly to the success of the meeting. It is also especially desired to thank Bernard Chaiken, of the Division of Physical Research, Bureau of Public Roads, for his assistance in assembling and organizing this report.

W. J. Halstead, Chairman  
Committee on Durability of Concrete—Chemical Aspects

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***Part I***

***Field Experience***

# Field Experience with Alkali-Aggregate Reaction in Concrete: Western United States

BAILEY TREMPER, Supervising Materials and Research Engineer,  
California Division of Highways

●IN THE absence of more specific delineation of the area to be covered by this discussion the author interpreted his assignment to include the area west of the Mississippi River. Accordingly, the information obtained pertains to the 20 states comprising this region. Later it was learned that a similar report covering the Central United States had been assigned to another author. Therefore, some overlap exists in the areas covered in the two reports.

To obtain the information needed a circular letter was sent to the Materials Engineers of the highway departments of the 20 Western States. The response was gratifying, in that replies were received from all but two states. The first question asked was:

Do you know of any construction within your state, consisting of highway pavements or structures or airport runways, in which the aggregates used have a proven record of unsatisfactory service with respect to the alkali-aggregate reaction when used with high-alkali cement and which have been used in concrete of other make-up which has given improved results in service?

No state in its reply volunteered information regarding runway construction. Therefore, the information obtained pertains only to highway structures and pavements.

Eleven states replied that no distress assignable to alkali aggregate had been observed in their states to their knowledge. However, three midwestern states referred to trouble with the cement-aggregate reaction, which they did not consider to be the same as the alkali-aggregate reaction.

The remaining seven states all reported distress from alkali-aggregate reaction. Highway pavements or structures were cited as evidence. An eighth state, Washington, that did not reply to the inquiry, is known from published reports to have experienced trouble. With the exception of Nebraska and part of Wyoming, all of the eight states lie west of the Continental Divide.

Additional information was requested from those states that answered the first question in the affirmative. These replies are summarized briefly in alphabetical order in the following:

Wayne O'Harra, reporting for Arizona, cited distress attributed to alkali-aggregate reaction in two pavements and numerous structures either known or believed to have been constructed with cements high in alkalies. For the past ten years all cement has been specified to contain less than 0.60 percent alkalies. Air entrainment was also started at the same time. During this period observations have shown that the methods of correction have been effective. He does not feel that field evidence alone proves conclusively that low-alkali cement, of itself, has been responsible for the observed improvement. However, mortar bar expansion tests in the laboratory show that low-alkali cement is effective in reducing expansion.

Alkali-aggregate reaction in California highway work has been extensive. Much of it has been reported in the literature and need not be repeated here. For the past 15 years the sole corrective measure has been the use of low-alkali cement. Many highly reactive aggregates containing either opal or intermediate igneous glass have been used. The results have been fully satisfactory, judging from fairly comprehensive field surveys.

L. F. Erickson referred to numerous bridges and pavements in southeastern Idaho that have been adversely affected by alkali-aggregate reaction. He mentioned specifically two structures near Pocatello built with cement that presumably contained about 0.74 percent alkalies ( $\text{Na}_2\text{O}$  equiv.). In 1944 a new structure using essentially the same aggregates was constructed with low-alkali cement ( $\text{Na}_2\text{O}$  equivalent, 0.53 percent).



A recent inspection at the age of 12 years shows no evidence of distress.

W. M. Carver, reporting for Nebraska, referred to the well-known experience in Kimball in which serious expansion developed in pavements within a year after construction. The aggregates were from local sources and the cement contained over 1.30 percent alkalis. There has been no construction with low-alkali cements and Kimball aggregates. Distress elsewhere in Nebraska is attributed to cement-aggregate reaction.

G. W. Harra of Oregon reported serious distress in a number of bridges in Malheur County that were constructed during 1927-28, during which time the available cement contained in excess of 1 percent of alkalis. The high alkali content during this period was due to a change in the shale being used. Previously the cement was believed to have been low in alkalis. Since 1930 the average alkali content has been about 0.4 percent. Virtually the same aggregates have been used in all construction. Except for construction during the 1927-28 period, the results have been satisfactory.

D. F. Larsen, reporting for Utah, stated that some distress had been observed in concrete in which gel relics have been found. However, unsound aggregate, and freezing and thawing have been factors. He is unable to differentiate clearly between the three possible causes of distress. No mention was made of corrective measures.

I. E. Russell stated that alkali-aggregate reaction has caused adverse results in structures in Laramie, Wyoming. The cement used contained between 1.3 and 1.4

percent alkalis and the aggregates were from the Laramie River. In 1945, curbs and gutters were constructed with Laramie River aggregates and a cement containing 0.66 percent alkalis. This work, now 11 years old, shows no evidence of adverse alkali-aggregate reaction.

No reply has been received from Washington, but the author can state from personal experience that six bridges built with Cowlitz River or White River aggregates, both containing Mt. Rainier andesite, and cements from two mills believed to have contained from 0.8 to over 1.0 percent alkalis, showed serious distress from alkali-aggregate reaction at an early date. Six other bridges, similarly situated, built with Cowlitz River aggregates and cements from two mills that were believed to have contained less than 0.6 percent of alkalis, showed no evidence of adverse alkali-aggregate reaction up to ages

of at least 20 years. As far as known, no type of corrective measure other than low-alkali cement has been attempted in Washington. The results of this survey show the following:

Of the twenty states lying west of the Mississippi River, alkali-aggregate reaction has been observed in highway work in eight of them. In one of these, Utah, evidence of distress from this cause is inconclusive, and results of corrective measures, if attempted, were not reported. Another state, Nebraska, has observed distress from alkali-aggregate reaction but has no knowledge of possible corrective measures in the field.

Six states reported that excellent performance of from 10 to 20 years has been obtained when low-alkali cement has been used with aggregates that have been clearly established by field experience to be reactive.

Idaho reported that distress occurred with a cement containing 0.74 percent  $\text{Na}_2\text{O}$  equivalent (assumed). Wyoming reported satisfactory results at the age of 11 years with reactive aggregates and a cement containing 0.66 percent alkalis (basis of computation not stated). In the remaining six states there appears to have been no experience with cements having alkali contents in the range of 0.6 to 0.8 percent.

None of the states reporting has had experience with corrective measures other than low-alkali cement. No information was developed concerning experience in airport runways.

TABLE 1  
SUMMARY OF REPLIES FROM 20 WESTERN STATES

State	No Reply	No Alkali-Aggregate Reaction	Cement-Aggregate Reaction	Alkali-Aggregate Reaction
Arizona				x
Arkansas		x		
California				x
Colorado		x		
Idaho				x
Iowa		x	x	
Kansas		x	x	
Louisiana		x		
Minnesota		x		
Nebraska			x	x
Nevada	x			
New Mexico		x		
North Dakota		x		
Oklahoma		x		
Oregon				x
South Dakota		x		
Texas		x		
Utah				x
Washington	x			x
Wyoming				x
Total	2	11	3	8

# Alkali-Aggregate Reaction in the Los Angeles Area

C.W. BEARDSLEY, Director, Bureau of Standards and Research;  
C.M. WAKEMAN, Director, Harbor Department Laboratory; and  
P.S. WRIGHT, Construction Materials Engineer,  
Department of Public Works, City of Los Angeles, California

●THE deterioration of concrete which results from the alkali-aggregate reaction was well known in Los Angeles prior to the exposition of the reason for it, which was published by T. E. Stanton in 1942. A viaduct over the Los Angeles River at 6th Street had been constructed about 1931 by the Department of Public Works. A reactive type of aggregate from Piru, Calif., was used for the reinforced concrete construction.

At the time Stanton propounded his explanation of the reaction, this large and expensive structure was in distress. Deterioration has been progressive, and the city has spent about \$150,000 for repairs and waterproofing during the past two years. It is hoped, by waterproofing the areas exposed to moisture, to partially inhibit the reaction and to prolong the useful life of the viaduct.

Other examples of reaction have appeared in many structures, such as the Ventura sea-wall, the Santa Barbara Mission, and several smaller buildings in the San Pedro-Long Beach areas.

The work which has been done by Sub-Committee III-d of Committee C-9 ASTM has been followed with much interest. The contributions of the many engineers and scientists who have worked on this problem are unquestionably of great value. Some of the means of identification of reactive aggregate which have been developed, although they are useful and reliable, are not suited to the needs of the Department of Public Works and Harbor Department of the City of Los Angeles. The ASTM Test for Potential Reactivity of Aggregates, C 289-54 T, has been found most useful and serviceable.

This viewpoint has been adopted for the following reasons:

1. Initiation and completion of numerous small construction contracts cannot await the results of expansion bar tests.
2. Petrographic examination requires the services of a trained petrographer and the reliability of the findings depends upon his training and skill. The judgment of the petrographer and the engineer are primary factors in the application of the petrographic study. This method therefore, does not lend itself to precise specification in contract documents.
3. The ASTM method (Test C 289-54 T) readily detects the reactive minerals which are common in this district, such as the opal and chalcedony of the Monterey formation. No special personnel is required. The procedure can be carried out by chemists who do other departmental testing. The test results are quantitative and can be made the subject of specification.

Though realizing the limitations of the Tentative Test for Potential Reactivity of Aggregates, C 289-54 T, the Public Works Department has chosen to rely upon it for exactly what it is intended to be: a potential indication of possibly reactive material.

4. Millions of tons per year of suitable materials are mined from the alluvial deposits of the Big Tujunga and San Gabriel Rivers. They all have a ratio, when tested by the C 289-54 T method, of approximately 0.25 to 0.35. They are used with normal alkali-content cement. No reactivity attributable to this aggregate has been observed.

Experience over many years has shown that aggregates from sources in the coastal range may contain reactive material. Aggregate from such sources, although indicated safe by the test for potential reactivity, is nevertheless limited to use in surface work and, in such use, low-alkali cement is required.

The foregoing limitations provide a satisfactory criterion that enables a prompt decision in regard to any aggregates proposed for use. Repetition of damage due to the alkali-aggregate is not anticipated. The Director of the Harbor Department Laboratories has banned the use of aggregates from areas in the Monterey formation where past use has indicated deleterious reaction.

# Field Experience with Alkali-Aggregate Reaction in Concrete: Central United States

W. E. GIBSON, Engineer of Tests, Kansas State Highway Commission

●THE sixteen states considered in the Central United States are Arkansas, Colorado, Illinois, Iowa, Kansas, Louisiana, Minnesota, Missouri, Nebraska, New Mexico, North Dakota, Oklahoma, South Dakota, Texas, Wisconsin and Wyoming. A questionnaire prepared and sent out to the states by the Highway Research Board Committee on Durability of Concrete—Chemical Aspects in 1953, revealed the following: Four states did not reply; eight states replied that they had no alkali reaction in concrete; two replied that possibly they may have alkali-reactive aggregates; and two replied that they did have alkali-aggregate reaction or cement-aggregate reaction in concrete. Therefore, these remarks are confined to the aggregate problem in the states of Iowa, Kansas, Missouri, and Nebraska, with emphasis on Kansas and Nebraska inasmuch as they replied that they had such a problem.

Probably the Kimball, Nebraska, aggregate is best known in this area for producing severe cracking, expansion, and loss in strength when used in concrete construction. This aggregate has been used in three concrete paving projects and one concrete railroad overpass in Kimball. The three paving projects had developed severe cracking and expansion, and the railroad overpass had visible cracking at five years of age. The records indicate at least three different brands of cement were used in the Kimball projects; however, no records seem to be available regarding the alkali contents of these cements.

In a study of special concrete problems in Kansas, Nebraska, Iowa, and Missouri, carried out as a cooperative project between the Portland Cement Association and Kansas State College, the Kimball aggregate was studied. In this study Kimball aggregate was used to mold a 24- by 24- by 6- in. concrete specimen using a low-alkali cement (0.55 percent  $\text{Na}_2\text{O}$  equivalent) for natural outside weathering. This specimen containing Kimball aggregate and low-alkali cement has severe cracking after fourteen years of natural outside weathering.

Aggregate from the Platte River in Nebraska has been used extensively in concrete pavements and structures in Nebraska. This aggregate has also been used in Iowa, Missouri, and Kansas. The service record of Platte River aggregate in concrete has varied from moderate cracking to severe cracking in the four-state area.

Aggregate from the Republican River in Kansas and Nebraska has produced severe cracking, expansion, and loss of strength when used as a single total aggregate in concrete. Concrete pavements and structure containing Republican River aggregate have been constructed in the Republican River watershed from Junction City, to St. Francis, Kansas. This aggregate has produced more severe cracking, expansion, loss of strength, and deterioration when used in concrete than any other aggregate in the state of Kansas to date. In this respect, it ranks next to the Kimball aggregate.

The bridge across the Republican River at St. Francis was constructed from aggregate adjacent to the bridge site. In a few years the bridge floor had expanded until it closed the expansion joints, crushed the bridge floor, and tore loose some of the steel diaphragm connectors between the steel girders. The concrete piers and pier caps cracked so badly that a repair job was necessary. The repairs to this bridge consisted of cutting and chipping the cracked, disintegrated concrete from the piers and pier caps and then guniting. The expansion joint and the bridge floor adjacent to the expansion joint was cut out and replaced. This bridge was constructed with no shear connectors between the bridge floor and the steel girders: to measure the expansion of the concrete relative to the steel girders it was necessary to find a point where a form tie wire had scratched the paint along the top of the steel girder. The bridge, constructed in 1936, showed the concrete expansion relative to that of the steel girders was over 0.22 percent by 1946.

The city of St. Francis, Kansas, built a water pumping plant using Republican River

aggregate in the concrete foundation for the engines. In approximately three years after the engine foundations had been placed, the concrete cracked, expanded, and warped until the engines were pushed out of line, causing damage to the engines. The original unreinforced foundations were taken out and replaced with reinforced concrete.

The railroad overpass at Almena, Kansas, was built with local aggregate from a dry pit near that town. The concrete pier caps on this structure cracked and deteriorated until it was necessary for the Kansas State Highway Commission to make repairs.

The Republican River aggregate has produced severe cracking in the concrete of the bridges across the Republican River at Scandia, Concordia, and Clay Center, Kansas. This aggregate, when used as a single aggregate in concrete construction with cements having an alkali content of less than 0.60 percent, has produced severe cracking, loss of strength, and warping where the concrete is exposed to outside natural wetting and drying. Republican River aggregate used as a single aggregate in construction of concrete culverts has not produced cracking or deterioration in the barrels of the culverts. Severe cracking occurs in the wingwalls and handrails of bridges and culverts in which this aggregate has been used. This condition also exists with Platte River, Kaw River, and Arkansas River aggregates, and with a number of aggregates from dry pits in this area. The only place where these reactive aggregates have produced severe cracking, loss of strength, and deterioration in concrete has been in that portion of the pavement or structure subjected to wetting and drying. The author has never seen this type of severe cracking in concrete pipe installed underground when the pipe was constructed with the aggregates from this area that have produced serious cracking in concrete pavements.

The Kaw River aggregate has produced severe cracking, expansion, and loss of strength when used in concrete construction from Junction City to Kansas City, Kansas, and the Arkansas River aggregate has a similar service record from Great Bend to Arkansas City, Kansas.

The State Highway Commission of Kansas was aware of this problem more than 25 years ago, and by field service records and laboratory wetting and drying tests has separated the servicable aggregates from the unservicable ones. Full-scale field projects, laboratory pilot projects, and laboratory specimens of concrete containing cements with less than 0.60 percent  $\text{Na}_2\text{O}$  equivalent have been built. After seven years of natural weathering, the concrete has severe cracking and loss of strength. Therefore, it appears that a specification limiting the alkali content of cements in this area to 0.60 percent  $\text{Na}_2\text{O}$  equivalent would not be a guarantee to stop this type of cracking. These results have led to the general conclusion that the expansive reaction with these aggregates differs from that for the aggregates on the West Coast and have led to the use of the term cement-aggregate reaction rather than alkali-aggregate. Kansas experience has been that use of the two present ASTM procedures, C 227-52 T and C 289-54 T, did not enable separation of the servicable aggregates from the unservicable aggregates.

The most economical and satisfactory method the Kansas State Highway Commission has found to stop this severe map cracking and loss of strength with these reactive aggregates is the addition of 30 percent durable, absorptive crushed limestone having a maximum size of 1 in. and a minimum size of No. 4 mesh.

A number of full-scale projects, pilot projects, and laboratory specimens in which the concrete aggregate consisted of 70 to 75 percent reactive aggregates and 25 to 30 percent crushed limestone by weight have been built. After 17 to 20 years the concrete has good strength (600 psi modulus of rupture), no map cracking, and a change in length of 0.025 per expansion.

The Supplemental Specification 45-256 prepared in 1946 is now incorporated in the Kansas Highway Commission Standard Specifications for State Road and Bridge Construction, Addition 1955, and appears under Section 93 of the 1955 Kansas Standard Specifications. It stipulates the requirements and test procedure covering the aggregates that have produced reactivity in concrete.

# Field Experience with Alkali-Aggregate Reaction in Concrete: Eastern United States

D.O. WOOLF, Chief, Concrete Branch, Division of Physical Research, Bureau of Public Roads

● THIS paper covers the failure of concrete pavements and bridges in the Eastern United States due to a chemical reaction between alkali ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) in the cement and soluble silica in the aggregate. The reaction, customarily known as the alkali-aggregate reaction, promotes excessive expansion and cracking of concrete. In itself, the cracking is more disfiguring than dangerous, but it does permit ready access of water to the interior of the concrete mass. Then the failure of the concrete by freezing and thawing, or by wetting and drying, may be greatly accelerated.

As early as 1930, concern was expressed over the number of concrete pavements and bridges in some of the southeastern states which showed expansion and multiple cracking. Several independent studies of the problem were made, but these were directed mainly toward the influence of magnesia in the cement on the soundness of the concrete. The reason for this association had been furnished by the performance of concrete pavement on the Travelers Rest Road in South Carolina. Within two years after this pavement was laid, excessive expansion and a well-defined crazing of the concrete built with one brand of cement was found. Analyses of the cement showed the magnesia content to be high, as much as 8 or 9 percent being found in some tests. As three other brands of cement had been used in this pavement with satisfactory results, and these cements contained low to moderate amounts of magnesia, it was believed that the magnesia content of cement was definitely associated with the durability of the concrete.



Figure 1. Cracking of concrete pavement in Georgia.

In 1934, the Bureau of Public Roads, with the assistance of the interested state highway departments, began an extensive study of the durability of concrete pavements and associated structures in the Southeastern States. Although only 8 percent of the 1,077 miles of concrete pavement inspected showed distress, many pronounced failures were found (see Figure 1). In the summary of the data collected, it was found that the failure of concrete was associated with the brand of cement used, or the combination of cement and aggregate. Efforts were made to determine whether the chemical analysis of the cement could furnish information as to the reason for the distress of the concrete. No complete analyses could be found. Usually, determinations were made for magnesia, sulfur trioxide, and loss on ignition, and occasionally for silica, lime, alumina, and iron oxide. No connection between

these chemical determinations and the failure of the concrete was found other than that for the one plant which furnished cement with a high magnesia content.

When Stanton published his report of the effect of alkali in cement, analyses for alkali content were made of cement from all mills which furnished cement used in the



Figure 2. Failure of concrete on US 1 in Dumfries, Virginia.

ity of concrete. It is now possible to state that the concrete placed during the last 10 years is of comparable quality with that in any other section of the country.

During the last few years, some concern has been given to reported failures of concrete prepared with low-alkali cement. In 1955 a survey was made of major bridge structures in Georgia which had been prepared with reactive aggregate and low-alkali cement. All of these bridges were six to seven years old, and it was expected that the concrete, if subject to an alkali-aggregate reaction, would show evidence of this. Although some portions of different bridges did show some faint pattern cracking, in no case could the cracking be stated to identify concrete subject to the alkali-aggregate reaction.

During this survey, failure of a bridge in Toccoa, Georgia, due to the alkali-aggregate reaction was observed. The aggregate was gravel from the Savannah River. Previously this aggregate had been considered nonreactive. In this bridge, high-slump concrete was used to permit its transportation in pipes for a considerable distance. It is believed that the alkali-aggregate reaction was promoted not only by the high-alkali cement but also by the wetness of the concrete.

Other than the failures of concrete in the highways, principally in Alabama, Georgia, and South Carolina, which are interrelated by use of similar cements and aggregates, no extensive failure of concrete in the Eastern States due to the alkali-aggregate reaction is known. Several individual structures might be mentioned, such as the Tuscaloosa Lock in Alabama, and the Buck hydroelectric plant in Virginia. The concrete in the Tuscaloosa Lock was reported (1) to have failed due to a chemical reaction between alkalis in the cement and chalcidonic chert aggregate. The Buck plant (2) was built in 1912 of concrete prepared with crushed phyllite (intermediate between slate and schist) and, presumably, a high-alkali cement. It is interesting that the report states the concrete was poured wet according to common practice at the time of construction.

In 1934, the pattern and behavior of cracking of concrete on US 1 in Dumfries, Va., was found to resemble closely that of failed concrete pavement in Alabama and Georgia.

concrete studied. It was found that the brands of cement which were associated with failure of concrete invariably had an alkali content of over 0.6 percent. Those used to prepare concrete in which little or no failure occurred had alkali contents of less than 0.5 percent.

Identification by source of all aggregates used was not entirely successful because in many cases a word was used to designate the aggregate and this word could denote either the name of a producer or the name of a town near several sources of aggregate produced by different companies. However, it soon became apparent that quartz gravels produced near the geographical center of Alabama were more definitely associated with distress of concrete than gravels from any other source. Concrete prepared with crushed stone showed little distress except when used with a high-magnesia cement. Blast furnace slag had the poorest record of all coarse aggregates; inasmuch as slag was usually used with high-alkali cements, the concrete prepared with these materials had the greatest possibilities of failure.

Reduction of the alkali content of the cement used in the Southeastern States has caused a great increase in the durabil-

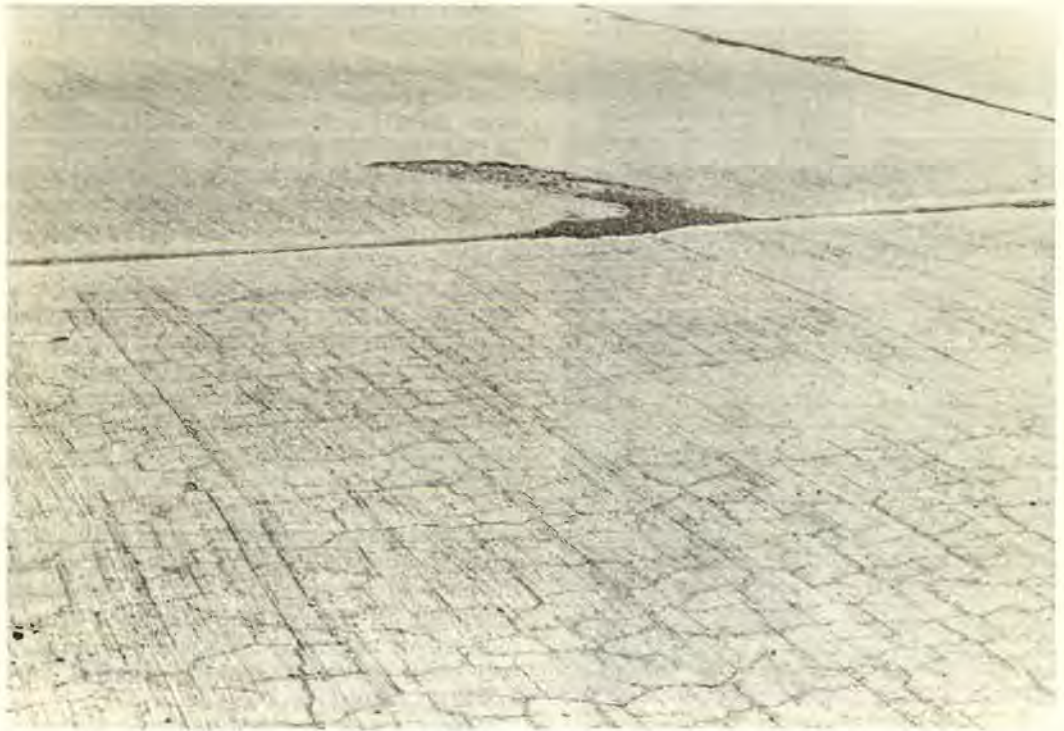


Figure 3. Failure due to alkali-aggregate reaction, Pentagon network.

This is shown in Figure 2. No samples of the concrete were obtained for examination, but it is believed that this concrete was subject to the alkali-aggregate reaction.

In 1957 cores were drilled from a badly cracked section (Figure 3) on the road network surrounding the Pentagon in Arlington, Va. The cores showed large amounts of gel present in the concrete, and it can be stated that the concrete failed due to the alkali-aggregate reaction. Although records fail to show the sources of the materials used, examination of the concrete showed the aggregate to be Potomac River gravel. The cement probably was from one of the mills in the vicinity of Washington, D.C., all of which produced cement with a fairly high alkali content. This is the first known instance of the positive identification of gel in concrete prepared with Potomac River gravel.

No other examples of the alkali-aggregate reaction are known in the Eastern States. In New Jersey many miles of concrete pavement built with dolomite coarse aggregate, quartz sand, and Lehigh Valley cements have developed a pattern of cracking similar to that in Alabama. Although many test specimens taken from this concrete have been examined, no positive evidence has been found that the alkali-aggregate reaction is involved. On Long Island, multiple cracking and great volume change have been found in concrete pavement containing local quartz sand and gravel. No studies of cores or samples from this concrete are known. It is believed, however, that this concrete would be much more liable to have been affected by the alkali-aggregate reaction than the dolomite concrete in New Jersey.

All along the Atlantic seaboard are many deposits of aggregate which are potentially reactive with the alkali in cement. It is possible that many occurrences of distress due to the alkali-aggregate reaction have not yet been identified. However, in many instances the concrete may be badly cracked but is still providing an adequate road surface for thousands of vehicles per day. It is suggested that ability to carry the imposed load without excessive repairs is far more important than the maintenance of an uncracked surface.

## REFERENCES

1. Mather, B., "Cracking of Concrete in the Tuscaloosa Lock." Proc., HRB, 31:218 (1951).
2. Kammer, H.A., and Carlson, R.W., "Investigation of Causes of Delayed Expansion of Concrete in Buck Hydroelectric Plant." Jour. Amer. Con. Inst., 12:6 (June 1941).



# Results of 1953 Questionnaire on Cement-Aggregate or Alkali-Aggregate Reaction in Concrete

● THE FOLLOWING questionnaire was circulated to all the state highway organizations, the various Corps of Engineers Divisions, and other interested organizations in 1953. The replies to this questionnaire are given in Table 1.

## QUESTIONNAIRE

1. Have you observed any concrete in your State or Division that is developing:
 

a. Alkali-aggregate reaction	Yes ( )	No ( )
b. Cement-aggregate reaction	Yes ( )	No ( )

(If the answer to question one part a. or part b. is yes, please answer as many of the following as you can; but if the answer is no, proceed to question 11.)
  
2. Which of the following characteristics develops in the concrete?
 

Loss of strength	( )	Scaling	( )
Expansion	( )	Blow-ups	( )
Contraction	( )	Exudations	( )
Cracking	( )	Other	( )

Remarks:
  
3. What types of structures were affected?
 

Pavements	( )	Structures	( )
Bridges	( )	Dams	( )
Handrails	( )	Others	( )

Remarks:
  
4. At what age is the reaction discernible? ( ) Years
5. At what ages does the reaction seem to stop? ( ) Years
6. What portions of the affected structures show the most reaction?
  - a. Where the concrete is damp and in the shade.
  - b. Where the concrete is dry and in the sun.
  - c. Where the concrete is damp with one or more surfaces dry and exposed to the sun.
7. Has the reaction been correlated with any characteristic of cement composition, and if so, to what characteristic of the cement?
8. Has the reaction been correlated with any characteristic of the aggregate?
 

Yes ( )	No ( )
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  - a. Name the rock types with which the reaction is associated.
  - b. Name any minerals occurring in the rocks, or separately, that are suspected of contributing to the reaction.
9. What corrective measures have been tried to retard or prevent the reaction?
10. Have any of the corrective measures been successful?
 

Yes ( )	No ( )
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  - a. If your answer to question 10 is yes, is your decision as to success based on laboratory or field experience? (\_\_\_\_\_)

b. If based on field experience, how many years experience? ( \_\_\_\_\_ )

11. What laboratory tests do you employ in aggregates or cements that are designed to avoid reaction?

- a.
- b.
- c.

12. What requirements are included in specifications for cement, aggregate, or construction to avoid reaction?

Reporting Agency	1a. Alkali-Aggregate Reaction	1b. Cement-Aggregate Reaction	2 Resulting Characteristics Developed	3 Structure Types Affected	4 Age Reaction Discernible, yr	5 Age Reaction Ceases, yr	6 Portion of Structure Showing Most Reaction	7 Reaction Correlated with Cement Characteristics
Alabama	Yes	Yes	Expansion, cracking, exudations, others	Pavements Bridges Handrails	4-8	7	Lighter parts of structure	No
Arizona	Yes	-	Expansion, cracking, loss of strength blow-ups, exudations	Pavements Bridges Handrails Structures Dams Others	2	Unknown	Where subject to wide temp & moisture content changes	Alkali Content
Arkansas	No	No	-	-	-	-	-	-
California	Yes	No	Expansion, cracking, exudations	Pavements Bridges Handrails Structures	1-5	7	Where damp with one or more dry surfaces exposed to sun	Alkali Content
Delaware	No	No	-	-	-	-	-	-
Florida	Yes	-	Cracking, expansion, blow-ups, exudations	Pavements Bridges	Unknown	Unknown	Concrete dry and in sun	Alkali Content
Georgia	Yes	-	Cracking, loss of strength expansion, exudations	Pavements Bridges Handrails	6	15 <sup>+</sup>	Alternate wet and dry	-
Idaho	Yes	Yes	Loss of strength expansion, cracking, scaling, blow-ups	Pavements Bridges Handrails	2	Unknown	Handrails Curbs Pier caps	Alkali Content
Illinois	No	No	-	-	-	-	-	-
Indiana (Purdue U.)	-	Yes	Expansion, cracking, blow-ups	Pavements Bridges Handrails	12-20	7	-	No
Kansas	-	Yes	Loss of strength, expansion, cracking	Pavements Bridges Handrails Structures	7	20 or more	Where damp with one or more dry surfaces exposed to sun	-
Kentucky	-	Yes	Cracking, scaling, blow-ups	Pavements Bridges Handrails Structures	-	-	-	No
Louisiana	No	No	-	-	-	-	-	-
Maryland	No	No	-	-	-	-	-	-
Massachusetts	No	No	-	-	-	-	-	-
Michigan	No	No	-	-	-	-	-	-
Minnesota	No	No	-	-	-	-	-	-
Missouri	Possibly	Don't know	Map cracking	Pavements Abutments Handrails	3-10	Unknown	Where damp on one side, no observation of effect of sun or shade	No
Nebraska	Yes	Yes	Loss of strength, expansion, cracking, blow-ups, exudations	Pavements Bridges Handrails Structures	5	10	Where damp with one or more dry surfaces exposed to sun	High alkali content
New Hampshire	No	No	-	-	-	-	-	-
New Jersey	-	Yes	Expansion, cracking, blow-ups, exudations	Pavements Bridges Handrails Structures	4	Unknown	Where damp and in shade, where damp with one or more dry surfaces exposed to sun.	No. Possible relation of high C <sub>3</sub> A (22%)
North Carolina	No	No	-	-	-	-	-	-
North Dakota	No	No	-	-	-	-	-	-
Ohio	No	No	-	-	-	-	-	-
Oklahoma	No	No	-	-	-	-	-	-

ON ALKALI-AGGREGATE REACTIONS IN CONCRETE BY HRB  
 CONCRETE—CHEMICAL ASPECTS

8	9a.	9b.	9	10	10a.	10b.	11	12
Reaction Correlated with Aggregate Characteristic	Rock Types Associated with Reaction	Mineral Types Associated with Reaction	Corrective Measures Employed	Corrective Measures Successful?	Success Based on Lab. or Field Experience	Years of Field Experience	Lab. Tests Designed to Avoid Reaction	Specification Requirements to Avoid Reaction
No	-	-	Low alkali cement, entrained air, pozzolans	?	-	-	Alkali content	0.6% max. alkali
Yes	Andesites	-	Low alkali cement, entrained air	Yes	Field	7	Alkali content	0.6% max. alkali
Yes	Opaline shales, intermediate volcanics	Opal, tridymite, volcanic glass	Low alkali content	Yes	Both	10	None Chemical analysis, mortar bars, petrographical & lithographical examination AASHTO, T-21-42 - organic impurities in sands for concrete	None Low alkali cement with reactive aggregates
Only with high alkali cement	Montgomery, Ala., or Tuscaloosa, Ala. aggregates (with high alkali cement)	-	Low alkali cement with these aggregates	Unknown	-	-	Alkali content	Less than 0.6% alkali with reactive aggregate
-	Chert gravel, granite, gneiss	Chalcedony, opal	Water proof painting	Reasonably	Field	6	Alkali content	0.6% max. alkali as Na <sub>2</sub> O
No	-	Cherts, obsidian, rhyolite	Low alkali cement	Yes	Both	10	Alkali content, expansion bars	Less than 0.6% alkali
-	-	-	-	-	-	-	None	None
No	Limestone	-	None	-	-	-	None	None
Yes	Granite, quartzite, calcite, basalt	Feldspar, quartz, mica, chalcedony, chert, silicates	Additions of crushed limestone	Yes	Both	15	Wetting and drying tests on concrete made with cement and aggregate for 12 months	3"x4"x16" beams in wetting & drying test shall not expand in excess of 0.05% at 180 days nor more than 0.07% at 365 days
No	-	-	None	-	-	-	-	-
-	-	-	-	-	-	-	None	None
-	-	-	-	-	-	-	None	None
-	-	-	-	-	-	-	None	ASTM Standard Specifications
-	-	-	-	-	-	-	Mortar Bars chemical analysis, ASTM potential reactivity of aggregates	None
-	-	-	-	-	-	-	None	None
Yes	Chert gravel, limestone	-	No chert gravel except in mass concrete	Don't know	-	-	Stanton's Mortar Bar Test	No chert gravel except in mass concrete
Yes	-	Opal	20-30% fly ash, 30% crushed limestone in aggregate	Yes	Both	7 (Limestone)	Mortar bar test, wetting and drying test of concrete beams, Bureau Recl. test for pot. reactivity of aggregates	No aggregate shall be used that will cause excessive expansion. Use of 30% limestone in concrete.
-	-	-	-	-	-	-	None	None
No	Dolomite	-	None	-	-	-	None	Dolomite not permitted
-	-	-	-	-	-	-	None	None
-	-	-	-	-	-	-	None	None
-	-	-	-	-	-	-	None	None
-	-	-	-	-	-	-	None	None

Reporting Agency	1a. Alkali-Aggregate Reaction	1b. Cement-Aggregate Reaction	2. Resulting Characteristics Developed	3. Structure Types Affected	4. Age Reaction Discernible, yr	5. Age Reaction Cesses, yr	6. Portion of Structure Showing Most Reaction	7. Reaction Correlated with Ceme Character
Oregon	Yes	Yes	Loss of strength, scaling, blow-ups, exudations	Bridges Handrails	5(10)	7	Where damp and in the shade	No
Pennsylvania	No	No	-	-	-	-	-	-
Rhode Island	No	?	Other (Complete disintegration of face and top of concrete curbing)	Poured-in-place and some pre-cast curbing	1	7	Where damp with one or more dry surfaces exposed to sun	No
South Dakota	No	No	-	-	-	-	-	-
Tennessee	No	No	-	-	-	-	-	-
Texas	-	Probably	Loss of strength, expansion, cracking, scaling, blow-ups	Pavements	5	Unknown	-	No
Utah	Yes	Yes	Expansion, cracking	Bridges Structures	2	7	Where damp with one or more dry surfaces exposed to sun	-
Virginia	Yes	-	Cracking, exudations	Pavements Handrails	Unknown	Unknown	Where damp and in shade	No
West Virginia	No	No	-	-	-	-	-	-
Wisconsin	No	No	-	-	-	-	-	-
District of Columbia	No	No	-	-	-	-	-	-
Missouri River Division Lab. Corps of Eng.	No	No	-	-	-	-	-	-
North Pacific Division Lab. Corps of Eng.	Yes	Yes	Expansion, cracking, scaling	Bridges Handrails Dams	Variable	Unknown	Where damp with one or more dry surfaces exposed to sun	No
South Atlantic Division Lab. Corps of Eng.	Yes	-	Expansion, cracking, exudations	Dams Lock Walls	4	Continuing	Where damp with one or more dry surfaces exposed to sun	Alkali content
South Pacific Division Lab. Corps of Eng.	Yes	-	Loss of strength, expansion, cracking, scaling, blow-ups, exudations, others	Pavements Bridges Handrails Structures Dams	1/2-10	7	-	Alkali
Southwestern Division Lab. Corps of Eng.	No	No	-	-	-	-	-	-
Waterways Experiment Station Corps of Eng.	Yes	Yes	Presence of reaction products as seen by microscope	Pavements Structures	Unknown	Unknown	Where damp with one or more dry surfaces exposed to sun	No data
Bureau of Reclamation, Department of Interior	Yes	Yes	Loss of strength, expansion, cracking, exudations	Pavements Bridges Handrails Structures Dams	2	Continuing	Where damp and in shade, where damp with one or more dry surfaces exposed to sun	Alkali content
National Sand and Gravel Association	Yes	Yes	Expansion, cracking, exudations	Pavements Bridges	4	Unknown	Where moisture is present	No data

No answers received from:  
 Colorado New Mexico  
 Connecticut New York  
 Iowa South Carolina  
 Maine Vermont  
 Mississippi Washington  
 Montana Wyoming  
 Nevada



***Part II***

***Laboratory Tests to Show  
Potential Reactivity of  
Aggregates***

# Physical Tests on Concrete and Mortar

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● RECOGNITION of the problem of alkali-aggregate reaction and the employment of a mortar-bar expansion test in the laboratory to develop data on potential reactivity of cement-aggregate combinations both date from Stanton's 1940 work (1). He discovered that mortar bars made with an aggregate that had given deleterious expansion in service, a high-alkali cement, and a highwater-cement ratio (0.94) stored in sealed cans over water at room temperature, would expand and develop cracks and exudations; but that the same aggregate with low-alkali cement, or the same cement with an aggregate of good service record, would not.

ASTM Committee C-1 on Cement formed a working committee on "Effects of Alkalies in Portland Cement on the Durability of Concrete" that prepared extensive summaries of data (2), carried out cooperative testing programs, and in 1950 sponsored the adoption of ASTM Designation C 227, Method of Test for Potential Alkali Reactivity of Cement-Aggregate Combinations (3). Stanton summarized his findings relative to the mortar-bar test in 1943 as follows (4): "Best over-all long-time results were obtained through curing in sealed containers at 70 F." He reported that 1- by 1-in. or 2- by 2-in. specimens expand most when stored in sealed containers over water, but larger specimens, 6- by 6-in. or 6- by 12-in., may expand more when immersed. He remarked: "Erratic behavior of reactive combinations has frequently been noted. . . discrepancies are probably due to lack of uniformity of ingredients, fabrication, or curing." The ASTM Working Committee in 1946 noted "many peculiar, anomalous, and sometimes conflicting results have been secured with this test." The cooperative program involved 10 laboratories, 5 aggregates, and 6 cements. The laboratory-to-laboratory range approached or exceeded the expansion; the laboratory-to-laboratory coefficient of variation declined with increasing magnitude of expansion.

As accepted in 1950 the mortar-bar test provided for aggregates to be graded (or crushed and graded) to provide 20 percent between each of 6 sieves, No. 4, 8, 16, 30, 50 and 100. The aggregates are made into a 1:2.25 mortar in 2-bar batches, using water to give a flow of 100-115 after twenty-five 1/2-in. drops in 15 sec. Bars made from this mortar are then moist cured in molds for 24 hr, stripped, measured, and stored at 100 F over water, read at 73.4 F after 16 hr or more cooling. The average of 4 specimens constitutes a test. As now in effect, the method has been changed to provide a mortar with a flow of 105-120 after ten 1/2-in. drops in 6 sec. This change, made in 1952, was based on results of further work by Stanton (5) in which he showed that the test could thereby be materially accelerated. ASTM Committee C-9 took cognizance of the applicability of the mortar-bar test to the evaluation of aggregates in 1952 when it revised its aggregate specifications C 33 to provide that "aggregates that have shown harmful reactions in concrete generally have produced expansions of more than 0.05 percent at 6 months or 0.10 percent at 1 yr when tested with a cement containing alkalies in excess of 0.8 percent expressed as sodium oxide." These comments were editorially modified in 1955 and then revised in 1956 to substitute 3 months for 6 months and 6 months for 1 yr based on a review of data developed using method C 227 as revised in 1952.

The Corps of Engineers, the Bureau of Reclamation and other agencies have used the mortar-bar test, not always following ASTM C 227. Bureau of Reclamation experience through 1948 was described by Mielenz and Witte (6). Work beginning in 1941 was discussed in 1946 by Blanks and Meissner (7) who recommended making bars from a mortar having a flow of 100-5 using ten 1/2-in. drops in 10 sec with sand graded as in concrete and a cement containing 1 percent or more alkalies. The Bureau of Reclamation procedure (6) involved a fixed grading: 19 percent between each of 6 sieves and 5 percent passing No. 100 for fine aggregates, 20 percent between the six sieves for crushed coarse aggregate. The mortar 1:2 and made in 3-bar batches to a fixed water-cement ratio of 0.40. The bars were stored at 70 F for 7 days, thereafter at 100 F.



The Corps of Engineers likewise began to use the mortar-bar test in 1941 and standardized its method in 1948 (8). It called for a 1:2.25 mortar made in 3-bar batches with a fixed water-cement ratio 0.5 and a fixed aggregate grading:

<u>Passing</u>	<u>Retained</u>	<u>Percent</u>
3/8 in.	No. 4	2.5
No. 4	No. 8	7.5
No. 8	No. 16	10.0
No. 16	No. 30	35.0
No. 30	No. 50	30.5
No. 50	No. 100	11.0
No. 100	-	3.5

The bars were moist cured in molds for 48 hr, stored at 100 F, read at 73.4 after 16 to 24 hr cooling. Nine specimens constitute a test.

In 1949, a cooperative study by all Corps of Engineers laboratories was begun, the results of which were published in 1956 (9).

In Phase I of this investigation, 8 test conditions were used by all laboratories: 2 cements (high- and low-alkali), 2 aggregates (reactive and nonreactive), and 2 mixing waters (distilled and tap). In Phase II there were also 2 cements and 2 aggregates but only 1 mixing water. The 4 mortars were prepared using 2 proportioning methods and the specimens were stored in 2 types of containers at 2 temperature conditions. All laboratories made specimens from all 4 mortars, but any one laboratory only used 2 of the other test conditions, except Waterways Experiment Station which used 3.

The results of these studies suggest the following:

1. Test results are not improved by use of distilled water for mixing mortar in preference to local tap water.
2. Continuing the measurements to a specimen age of 1 year is sufficient.
3. Aggregate combinations with low-alkali cement generally give more variable results than do those with high-alkali cement.
4. Mortar specimens containing reactive aggregate generally give smoother curves for length change versus time than do those with nonreactive aggregate.
5. Specimens made from mortar proportioned to constant flow (variable proportions) generally give less variable results than those proportioned to constant weights of all ingredients (variable flow).
6. Storage at high temperature (100 F) with length changes measured at normal temperature (73.4 F) gave larger and more uniform expansion results than both storage and measurement at high temperature.

The Corps of Engineers test procedure (CRD-C 123) is being revised essentially to follow ASTM Designation C 227, except that CRD-C 123 continues to provide for the use of an aggregate grading such as would be used in concrete.

Careful and detailed studies of the mortar-bar test have also been made by other agencies, notably the National Bureau of Standards (24), the Portland Cement Association, the Bureau of Public Roads (26), the Building Research Station in England, the Commonwealth Scientific and Industrial Research Organization in Australia, and the Danish National Institute of Building Research (27).

Building Research Station work beginning in 1946 was summarized by Jones and Tarleton in 1952 (10). Their procedure involved the use of the 19, 19, 19, 19, 19, 5 grading, a 1:2 mortar, one water-cement ratio determined by trial to give full compaction without bleeding and another higher w/c, stored at 20 C. One difference in procedure was the careful avoidance of mold oil or grease to permit more valid studies of surface phenomena. Their results indicate that high quality (low w/c) mortars should not be used. They recommended observations of condition of bars and suggest that such observations "form a valuable qualitative criterion and may lead to earlier assessment of reactivity than would measurement of expansion."

Perhaps the most extensive studies have been made in Australia by Vivian and Associates, reported in a series of publications beginning in 1943. In one paper (11)

results of tests on "composite" mortar bars showed that alkalis move from zones of high concentration to those of lower concentration. In others, results were given showing that: (a) expansion decreases with increasing porosity of mortar; (b) tensile strength of mortars are reduced by reaction before the expansion becomes high; (c) carbonation or drying can prevent alkali-aggregate reaction expansion; (d) expansion results from a swelling of the reactive aggregate particles; (e) expansion depends on amount of available water and on amount of reactive material present when its amount is small but decreases when the amount is large; (f) elevated temperatures increase initial rate of expansion but decrease total expansion; (g) expansion increases with decreasing particle size of reactive component except that very fine particles do not cause expansion; (h) there is a correlation between number and width of cracks and amount of expansion.

Recent summaries include those by Cook (23) and Thorvaldson (12) in 1952, Lerch in the 1953 ASTM Proceedings (13), and Lea (14) in 1956.

A large number of other testing and research procedures have been tried, and many described, that properly should be included under this item in that they are laboratory tests involving mortar or concrete and depend on measurement of physical properties. The only one standardized by ASTM is the Conrow Test (ASTM C 342) based on studies by Conrow (15) and a cooperative study by ASTM C-9, Subcommittee II-b, reported by Mielenz (16). Mortars are made as in C 227 but in 3-bar batches and to a flow of 100-115 in twenty-five  $\frac{1}{2}$ -in. drops in 15 sec stored immersed in a limited amount of distilled water at 73.4 F except for a 14-day period after the specimens are 28 days old when they are stored for 7 days at 131 F in the containers and then oven dried at 131 F for 7 days. This procedure has caused abnormal expansion with certain combinations of aggregate and cements of less than 0.6 percent alkalis that have given such abnormal expansion in Kansas and Nebraska.

The cooperative program also studied a wetting and drying test of concrete proposed by Scholer (17) but it has not been standardized by ASTM. A somewhat similar procedure was used by the Bureau of Reclamation (6) and has been standardized by the Corps of Engineers (18). Results of additional work were reported by Scholer and Smith (19).

Other procedures that have been proposed and described include the mason-jar test proposed by Woolf and Smith (20), the bi-aggregate slab warping test (21), tensile strength tests (11), determinations of dynamic modulus of elasticity (4).

Other minor variations of the mortar-bar test have been employed; for example, Carlson (22) reported tests of 6-in. bars.

Powers and Steinour (25) presented an interpretation of many results previously regarded as anomalous based on the following hypothesis:

Amorphous silica has structural discontinuities that lead to surface reaction with alkalis to yield an alkali-silica product when lime is unable to diffuse to the reaction site fast enough to form the lime-alkali-silica product. Expansion occurs when the alkali-silica product imbibes water. The alkali-silica product will not form when the silica particle is sufficiently small or the ratio of absorbed lime to alkali in the layer of reaction product is sufficiently high, the ratio being a function of alkali content of the external solution. Hence, excessive expansion occurs when the amount of reactive constituent and its particle size, and the amount of alkali in the cement, interact in a favorable environment to produce the alkali-silica reaction product and it, in turn, imbibes water.

#### REFERENCES

1. Stanton, T. E., Proc., ASCE, 66:10, 1781, (1940).
2. Appendix to Report of Committee C-1, ASTM Proc., 43:199 (1943); ASTM Bulletin 142, p. 28 (Oct. 1946).
3. ASTM Book of Standards, Part III.
4. Stanton, T. E., ASTM Proc., 43:875 (1943).
5. Stanton, T. E., ASTM Proc., 51:1087 (1951).
6. Mielenz, R. C. and Witte, L. P., Proc., ASTM, 48:1071 (1948).
7. Blanks, R. F. and Meissner, H. S., Proc., ACI, 42:517 (1946).
8. Handbook for Concrete and Cement, CE, WES, Vicksburg, Miss., Item CRD-C 123.48.

9. Report No. 2, TM 6-368, CE, WES, Vicksburg, Miss. (Sept. 1956).
10. Jones, F.E. and Tarleton, R.D., National Building Studies, Res. Paper No. 17.
11. Studies in Cement Aggregate Reaction, I through XXIV, 1947 through 1955.
12. Thorvaldson, T., "Chemical Aspects of the Durability of Chemical Products." 1952 Symposium on the Chemistry of Cements (London), p. 436.
13. Lerch, W., "Significance of Tests for Chemical Reactions of Aggregates in Concrete." ASTM Proc., 53:978 (1953); also ASTM STP 169, p. 334 (1956).
14. Lea, F.M., The Chemistry of Cement and Concrete, p. 493, St. Martins Press, New York (1956).
15. Conrow, A.D., ASTM Proc., 52:1205 (1952).
16. Appendix to Report of Committee C-9, ASTM Proc., 54:356 (1954).
17. Scholer, C.H., ASTM Proc., 49:942 (1949).
18. "Method of Test for Resistance of Concrete Specimens to Rapid Heating in Air and Cooling in Water." CRD-C 40-55, Handbook for Concrete and Cement, CE, WES, Vicksburg, Miss.
19. Scholer, C.H. and Smith, G.M., ASTM Proc., 54:1165 (1954).
20. Woolf, D.O. and Smith, T.R., ASTM Proc., 48:1108 (1948).
21. Alderman, A.R., et al, Jour. Counc. for Sci. and Ind. Res. (Australia). 18:4, 433 (1945).
22. Carlson, R.W., Jour. Am. Conc. Inst., 40:205, (1944).
23. Cook, H.K., "The Reaction of Alkalies in Cement with Certain Constituents of Mineral Aggregates." Proc., Int. Symposium on the Reactivity of Solids, p. 653, Gothenburg, Sweden, (1952).
24. Kelly, T.M., et al, Proc. Am. Conc. Inst., 45:57 (1949).
25. Powers, T.C., and Steinour, H.H., Proc., Am. Conc. Inst., 51:497 and 785 (1954-55).
26. Woolf, D.O., Public Roads, p. 50, (Aug. 1952).
27. Poulsen, Ervin, Proc., Am. Conc. Inst., 51:812-6 (1955).

### *Discussion*

R. C. MIELENZ, Director of Research, Master Builders Research Laboratories, Cleveland, Ohio—Mather's paper covers the subject very well. Referring to the third paragraph, it is important to note that for fine aggregates, Method C 227 does not stipulate a grading; it is required that the aggregate be tested "in a grading meeting the requirements of the specifications for the project." The grading on coarse aggregate is an expediency so as to permit testing of the coarse aggregate in a mortar.

Method C 227 is a test of a "cement-aggregate" combination rather than a test of an aggregate. As applied by some laboratories, the analogous procedure is directed to the evaluation of potential reactivity of an aggregate. Hence, a standard high-alkali cement and a standard grading is used so as to remove these factors as variables. Consequently, data from previous tests can be used quantitatively to evaluate the reactivity of a new aggregate.

For example, in current Bureau of Reclamation practice in evaluation of aggregates, the mortar bars are 1- by 1- by 10-in.; the sand is graded 20 percent by weight each of Nos. 4-8, 8-16, 16-30, 30-50, and 50-100; mix parts are 1:2 by weight; water-cement ratio is 0.40 by weight; and the bars are stored 24 hr at 70 F and thereafter at 100 F. The cement is a high-sodium type with alkali content approximating 1.2 percent, expressed as equivalents of sodium oxide.

Referring to Mather's discussion of the effect of particle size of alkali reactive constituents in aggregate on expansion of mortar, the expansion increases with decreasing particle size for opal, but the reverse is true for aggregates in which the reactive particles are only moderately active (1).

As a more general point, it would be well to refer to possible deficiencies of the mortar bar test as a means to evaluate alkali reactivity of concrete aggregate. These deficiencies may be grouped as follows:

1. Possible non-linear expansion of the specimens, such that expansion at 6 months, as now stipulated in Method C 227, is not indicative of the expansion to be found at somewhat greater age (2, 3).

2. Possible lack of significant expansion in Method C 227 in spite of development of deleterious alkali-aggregate reaction in the field; for example, the experience with certain gravels in Alabama.

3. Lack of adequate procedure to test the alkali-reactivity of coarse aggregate.

4. Miscellaneous procedural difficulties, such as maintaining a stock of a standard cement, variation in reactivity with aging of a particular sample of cement, repeatability, and variation from laboratory to laboratory.

It should be realized that mortar tests or even tests of concrete do not provide entirely satisfactory means to evaluate the potential alkali reactivity of concrete aggregate.

As indicated elsewhere (4) the writer remains unconvinced that a correlation is possible between deleterious expansion of mortar bars and the chalcedony content of the cherts as indicated by an index of refraction below 1.54. No data have been presented to show that the opal content of chalcedonic cherts can be determined from the index of refraction, or that opal need be present in chalcedony or microcrystalline to cryptocrystalline quartz to cause them to be deleteriously alkali reactive. Such electron diffraction data as are available do not support the view that opal is present in chalcedonic and quartzose cherts in a state of subdivision below the limit of resolution of the optical microscope (5). Rather, an index of refraction less than the mean of the indices of refraction of quartz is indicated to result from the presence in chalcedonic and quartzose cherts of minute water-filled voids not visible under the optical microscope. However, alkali reactivity of these cherts is not related in any simple manner to the abundance of such voids.

Microcrystalline to cryptocrystalline quartz with an index of refraction above 1.54 (say 1.547) can be equally or more alkali reactive than chalcedonic phases whose index of refraction is below 1.54. Experience with a type of chert from Hot Springs, Ark., designated as novaculite, is convincing in this respect (4). This chert is composed entirely of microcrystalline to cryptocrystalline quartz with a mass index of refraction of 1.547. Loss on ignition is 0.13 percent, in contrast to loss on ignition up to 1.70 percent in other non-opaline cherts studied. The identification of the silica as quartz is corroborated by X-ray diffraction and differential thermal analysis.

After careful study of concrete examined previously and described by Brown (6), the writer became convinced also of the occasional deleterious activity of certain phases of coarsely crystalline quartz. These studies do not corroborate the conclusion that the distress and gel in this concrete can be ascribed to chalcedonic cherts, although particles of such cherts are present in minor proportions in the aggregate.

A major need at this time is a correlation between petrography and alkali-reactivity of chalcedonic and quartzose cherts.

#### REFERENCES

1. McConnell, D., Mielenz, R.C., Holland, W.Y., and Greene, K.T., "Cement-Aggregate Reaction in Concrete." *Proceedings*, 44:93-128 (1947).
2. Hanna, W.C., "Discussion of Reactive Aggregate Combinations." *Proc., ASTM*, 43:894-897 (1943).
3. Hanna, W.C., "Aggregate Chemical Reactions of Aggregates in Concrete and a Suggested Corrective." *Proc., ASTM*, 47:986-999 (1947).
4. Mielenz, R.C., "Petrographic Examination of Concrete Aggregate." *Proc., ASTM*, 54:1188-1218 (1954).
5. Folk, R.L., and Weaver, C.E., "The Texture and Composition of Chert." *Amer. Jour. Sci.*, 250:498-510 (1952).
6. Brown, L.S., "Some Observations on the Mechanics of Alkali-Aggregate Reaction." *ASTM Bull.*, No. 205, 40-44 (1955).

# Chemical Tests for Alkali Reactivity of Concrete Aggregate

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● EARLY studies of alkali-aggregate reaction in mortar and concrete demonstrated conclusively that the expansion and general distress were caused by the process of chemical reaction or the products resulting from reactions between certain siliceous constituents of aggregates and the alkalis (sodium and potassium) released during the hydration of portland cement. Hence, it was concluded by many investigators that the potential deleteriousness of aggregates could be predicted, at least qualitatively, by chemical testing of aggregates in alkaline solutions.

Two manifestations of such chemical reactions could be observed; namely, the effect of the solution upon the aggregate and the effect of the aggregate upon the solution.

## ATTACK OF ALKALINE SOLUTIONS ON AGGREGATES

The stability of aggregate materials in alkaline solutions was determined by many investigators by immersion of prepared samples in such solutions as sodium, potassium, and calcium hydroxides; sodium and potassium sulfates; sodium and potassium carbonates; and mixtures of these substances (1, 2, 3, 4, 5). Among these solutions, those containing only sodium hydroxide are usually most destructive; those containing potassium hydroxide are usually somewhat less so.

The degree of attack effected on the sample can be evaluated by weight loss or degree of etch on polished surfaces. Very highly reactive substances (such as opal) suffered greatest dissolution in these tests, but deleteriously alkali-reactive substances of moderate susceptibility frequently showed less weight loss or lesser etching than did some innocuous aggregates. Innocuous glassy basalts are especially significant in production of such apparently anomalous behavior. In some instances, highly deleterious aggregate types gain weight while immersed in sodium hydroxide solutions. Also, some carbonates are dissolved slowly in strongly alkaline solutions and so show weight loss or etch which is totally unrelated to distress of concrete.

Such tests demonstrate that the degree of dissolution effected in aggregates by alkaline solutions cannot be used alone to estimate potential deleteriousness of concrete aggregate.

## CHANGE OF ALKALINE SOLUTIONS DURING THEIR ATTACK ON AGGREGATES

Investigators at the engineering laboratories of the Bureau of Reclamation studied the effects produced in alkaline solutions by the action of aggregate material (6). The changes in the solutions were measured as the concentration of substances in solution (particularly silica) and changes in alkalinity. When held in intimate contact with rock and mineral substances, water typically becomes slightly or moderately alkaline (7), but tests of a wide range of innocuous and deleterious rocks, minerals, sands, and gravels prove that this type of instability is not related to the reactivity with cement alkalis. Similarly, the resistance to change of pH of aqueous slurries of aggregate materials by addition of acids or bases was found to be unrelated to deleteriousness of the aggregate in mortar or concrete.

Several investigators determined the concentration of new substances in solution at completion of the tests. Alkalis were found to be released from some aggregates while they are immersed in caustic solutions (2), but this release is not related to the reaction which results in expansion of mortars and concrete. Similarly, release of  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{SO}_3$  into various alkaline solutions is not indicative of deleteriousness (5). Even the concentration of silica dissolved by alkaline solutions is not related directly to deleteriousness (6). Although the highly deleterious substances release large quantities of silica into strongly alkaline solutions, some innocuous materials liberate more silica than do some moderately deleterious aggregates.

Hence, it is concluded that change of alkaline solutions while they are in contact with an aggregate provides alone no basis for estimating potential deleteriousness of concrete aggregate.

#### QUICK CHEMICAL TEST FOR ALKALI REACTIVITY OF CONCRETE AGGREGATE

The previously cited experience suggested that the kind of chemical reactivity controlling alkali-aggregate reaction in concrete depends simultaneously upon the susceptibility of the constituents of the aggregate to attack by alkaline solutions and the concomitant change effected in the solution. In 1947, Mielenz, Greene and Benton (6) described a procedure depending simultaneously upon determination of: (a) the concentration of silica dissolved from a prepared sample of aggregate by a 1N NaOH solution during a prescribed procedure; and (b) the reduction produced in the alkalinity of the solution as determined by titration. They concluded that a deleterious degree of alkali reactivity of aggregate depended first upon the susceptibility of the constituents of the aggregate to release of alkali-soluble silica and, second, upon the efficiency with which the alkalies were utilized during the reaction in the production of alkalic silica gels capable of producing swelling or osmotic pressure when confined by portland cement paste.

The concentration of silica developed in the solution may be taken as an index to the reactivity of the aggregate, whereas the reduction of alkalinity is a measure of the decrease in potency of the solution and decline in its ability to continue the liberation of silica in water-soluble form.

The procedure has been applied widely in laboratories. In 1952 the American Society for Testing Materials formulated the Tentative Method of Test for Potential Reactivity of Aggregates: Chemical Method (ASTM Designation C 289) (8) on the basis of the procedure and details of technique developed in cooperative tests sponsored by the Corps of Engineers (9).

The originators of the test published data for more than 100 aggregates whose deleterious or innocuous character had been established by experience in structures, mortar tests, or petrographic examination (6, 10). The innocuous aggregates were separated from the deleterious aggregates by results of the test but the magnitude of expansion produced by the deleterious aggregates in mortar or concrete was not indicated reliably. Also, as would be expected, highly porous materials composed of alkali reactive substances were indicated to be deleterious by the chemical test even though the aggregate produced no deleterious effects in concrete or mortar.

In addition, certain substances, primarily magnesian carbonates and certain silicates (such as antigorite), were found to cause a reduction of alkalinity not related to alkali-aggregate reaction. Accordingly, some deleterious combinations of dolomite or antigorite and opal were indicated to be innocuous by the chemical test. Moreover, in the presence of alkali-soluble silica, calcite (the main constituent of limestone and marble) can cause an extraneous reduction of alkalinity and the silica concentration may be anomalous also. Finally, in spite of much work, both by the Corps of Engineers and under the sponsorship of Subcommittee II-b, ASTM Committee C-9, the test is not as reproducible as is ordinarily considered desirable for tests as a basis for engineering specifications.

Recent work by the Bureau of Reclamation (11) explored the sources of error in the test and supplied a basis for continued research, particularly in use of agitation during the reaction period, modification of the filtration procedure, and in determination of the reduction in the concentration of alkalies (sodium and potassium) in lieu of the reduction of titratable hydroxyl. These changes improve reproducibility and remove anomalous effects of magnesian carbonates and hydrous silicates. The work demonstrated the desirability of petrographic examination of aggregate as a means of evaluating the results of the test.

#### CONCLUSIONS

1. Chemical tests involving interaction of aggregate materials and alkaline solutions indicate potential alkali reactivity of the aggregate in concrete or mortar only if both the dissolution of silica and reduction of alkali concentration are measured.

2. By their nature, chemical tests do not evaluate certain physical characteristics of an aggregate, such as porosity and particle-size distribution.

3. Chemical tests are of continuous interest because, if properly designed, they are quick, low in cost, and require a minimum of material.

4. The most widely employed chemical test for alkali reactivity of concrete aggregate (ASTM Method C 289-54T) is useful as a preliminary means to evaluate potential alkali reactivity of concrete aggregate, particularly if facilities or time do not permit performance of a mortar test, such as ASTM Method C 227 (12). Nevertheless, the method is not as reproducible as is ordinarily desirable and anomalous results are obtained with certain lithologic combinations, namely:

(a) Magnesian and ferrous carbonates and some hydrous magnesian silicates (such as antigorite) cause an extraneous reduction of titratable hydroxyl ion, but this effect can be avoided by analysis of the solution for sodium and potassium in lieu of the titration to determine the titratable hydroxyl.

(b) Calcium carbonate can produce anomalous values of reduction of alkalinity (or alkali concentrations) and silica concentration; these effects are minor and probably will rarely cause erroneous conclusions on the potential alkali reactivity of an aggregate.

5. It is recommended that the technique of the quick chemical test (ASTM Method C 289-54T) be modified so as to require analysis for alkalis in lieu of titration and that consideration be given to the application of continuous agitation of the reaction vessels during the reaction period and modification of the filtration technique as means to improve reproducibility. Results of the chemical test should be correlated with petrographic examination to evaluate possible extraneous effects of certain rocks and minerals.

6. In considering the experience with ASTM Method C 289 it should be kept in mind that at present there exists no completely reliable and satisfactorily reproducible procedure to determine the potential alkali reactivity of concrete aggregate.

#### REFERENCES

1. Stanton, T. E., "Studies to Develop an Accelerated Test Procedure for the Detection of Adversely Reactive Cement Aggregate Combinations." Proc., ASTM, 43: 875 (1943).
2. Bureau of Reclamation, "Alkalies in Cement and Their Effect on Aggregates and Cement." U.S. Department of the Interior, 229 pp. (1942).
3. Stanton, T. E., Porter, O. J., Meder, L. C., and Nichol, A., "California Experience with the Expansion of Concrete Through Reaction Between Cement and Aggregate." Proc., Amer. Conc. Inst., 38:209 (1942).
4. Parsons, W. H., and Insley, H., "Alkali Etching Tests on Concrete Aggregates." Proc., Amer. Conc. Inst., 40:229 (1944).
5. Bean, L., and Tregoning, J. J., "Reactivity of Aggregate Constituents in Alkaline Solutions." Proc., Amer. Conc. Inst., 41:37 (1944).
6. Mielenz, R. C., and Greene, K. T., and Benton, E. J., "Chemical Test for the Reactivity of Aggregates with Cement Alkalies: Chemical Processes in Cement-Aggregate Reaction." Proc., Amer. Conc. Inst. 44:193 (1947).
7. Stevens, R. E., "Studies on the Alkalinity of Some Silicate Minerals." U.S. Geol. Surv., Prof. Paper 185-A, (1934).
8. Amer. Soc. for Testing Materials, "ASTM Book of Standards." Part 3, 1206 (1955).
9. Waterways Experiment Station, Corps of Engineers, U.S. Army, "Tests for Chemical Reactivity Between Alkalies and Aggregate, Report No. 1—Quick Chemical Tests." Waterways Experi. Sta. Tech. Memo. No. 6-368 (1953).
10. Mielenz, R. C., and Witte, L. P., "Tests Used by the Bureau of Reclamation for Identifying Reactive Concrete Aggregates." Proc., ASTM, 48:107 (1948).
11. Mielenz, R. C., and Benton, E. J., "Evaluation of the Quick Chemical Test for Alkali Reactivity of Concrete Aggregate (ASTM Method C289)." HRB Bull. 171, p. 1-15 (1958).
12. Amer. Soc. for Testing Materials, "ASTM Book of Standards." Part 3, 47 (1955).

# Petrographic Examination of Concrete Aggregate To Determine Potential Alkali Reactivity

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● PETROGRAPHIC examination of concrete aggregate is visual examination and analysis of the material in terms of both lithology and properties of the individual particles. Procedures of the examination are described in detail in "Recommended Practice for Petrographic Examination of Aggregates for Concrete (ASTM Designation, C 295 (1)). Petrographic examination is of great value in the determination of potential deleterious reactivity of individual samples of aggregate with alkalis released during the hydration of portland cement, but there are many other applications as well. These have been discussed previously (2).

## DISCOVERY OF DELETERIOUSLY ALKALI-REACTIVE ROCKS AND MINERALS

Following the identification in 1939-40 of alkali-aggregate reaction by Stanton (3) as a phenomenon separable from other processes by which concrete deteriorates, the rocks and minerals participating in the deleterious actions were identified by various means, as follows:

1. The deleteriousness of certain types (such as opaline shales, cherts, and calcareous rocks in the aggregates of the Salina Valley, California) was recognized by the correlation between the presence of particles of such materials in the aggregate and evident distress of structures and laboratory specimens.
2. Reaction rims on aggregate particles and gel, cracking, and popouts related spacially to particles of specific rock and mineral types, revealed the identity of the offending materials.
3. Laboratory studies of concrete and mortar containing selected rock and mineral types catalogued the range of expansion to be expected as a result of alkali-aggregate reaction involving specific substances.

## DELETERIOUSLY ALKALI-REACTIVE ROCKS AND MINERALS

Based on studies under way for the past 16 years, the potentially deleterious rocks and minerals and synthetic substances can be listed as in Table 1. The most important deleteriously alkali-reactive rocks

are: Opaline cherts, Chalcedonic cherts, Quartzose cherts, Siliceous limestones, Siliceous dolomites, Rhyolites and tuffs, Dacites and tuffs, Andesites and tuffs, Siliceous shales, Phyllites, Siliceous slates, Opaline concretions, Fractured, strained, and inclusion-filled quartz and quartzites.

### Opal and Opaline Rocks

Opal is the most alkali-reactive of all minerals. Aggregates containing as little as 0.25 percent by weight of opal should be considered to be deleteriously reactive under ordinary conditions of exposure. Opal is a common constituent of cherts, volcanic rocks and tuffs, and some shales, sandstones, concretions, limestones, coating materials on aggregate, and weathered rocks. It may constitute the entirety

TABLE 1

ROCKS MINERALS AND SYNTHETIC SUBSTANCES  
POTENTIALLY DELETERIOUS AS CONCRETE AGGREGATES

Reactive Substance	Chemical Composition	Physical Character
Opal	SiO <sub>2</sub> . nH <sub>2</sub> O	Amorphous
Chalcedony	SiO <sub>2</sub>	Microcrystalline to cryptocrystalline; commonly fibrous
Certain phases of quartz	SiO <sub>2</sub>	(1) Microcrystalline to cryptocrystalline; (2) Crystalline, but intensely fractured, strained, and/or inclusion-filled
Cristobalite	SiO <sub>2</sub>	Crystalline
Tridymite	SiO <sub>2</sub>	Crystalline
Rhyolitic, dacitic, latitic, or andesitic glass or cryptocrystalline devitrification products	Siliceous, with lesser proportions of Al <sub>2</sub> O <sub>3</sub> , Fe <sub>2</sub> O <sub>3</sub> , alkali earths, and alkalis	Glass or cryptocrystalline material as the matrix of volcanic rocks or fragments in tuffs
Synthetic siliceous glasses	Siliceous, with lesser proportions of alkalis, alumina, and/or other substances	Glass



of the rock or it may be present only in segregated masses, voids, fractures, or encrustations. It is easily recognized by its vitreous to waxy luster, conchoidal fracture, isotropic character, and low index of refraction (1.40 to 1.46).

### Chalcedony and Chalcedonic Rocks

Chalcedony is a cryptocrystalline to microcrystalline form of silica having the crystallographic structure of quartz but being characterized by a range of index of refraction (1.53 to 1.54) less than that of quartz (1.544 to 1.553) and a small weight loss on ignition (on the order of 1 or 2 percent). The water lost during ignition is absorbed at the edges of the silica lattice or is combined in the lattice as a proxy for silica tetrahedra (4). Specimens studied show a very weak differential thermal response at the inversion of  $\alpha$  to  $\beta$  quartz.

Chalcedony may occur as microcrystalline fibrous forms or as cryptocrystalline masses. It is the predominant constituent of most cherts and siliceous phases of cherty limestones and dolomites; it is common in shales, phyllites, slates, and volcanic rocks.

### Microcrystalline to Cryptocrystalline Quartz

Microcrystalline to cryptocrystalline quartz grades imperceptibly to chalcedony, on the one hand, and to fine-grained quartz on the other. Indeed, all three of these materials commonly are intermixed. This type of quartz is distinguished from chalcedony only by arbitrary criteria. Mather (5) suggests a limiting value for index of refraction of 1.54, that of chalcedony being lower than this limit. This value is acceptable, but its arbitrary nature should be recognized. The mean or mass index of refraction of microcrystalline to cryptocrystalline quartz is usually in the range 1.541 to 1.547. Loss on ignition is in the range 0.1 to 1.7 for specimens studied by the author. The differential thermal response at the  $\alpha$  to  $\beta$  quartz inversion is widely variable from specimen to specimen, the result bearing no evident relationship to loss on ignition or expansion of mortar bars containing high-alkali cement.

An aggregate should be considered to be potentially deleteriously reactive if it contains more than 5 percent by weight of chalcedony and/or microcrystalline to cryptocrystalline quartz. In the estimate of potential alkali reactivity, no distinction can be made in general between chalcedony and the microcrystalline to cryptocrystalline quartz. Of the chalcedonic and quartzose cherts tested in the engineering laboratories of the Bureau of Reclamation, a novaculite from Hot Springs, Ark., produced greatest expansion in a mortar test similar to ASTM Method C 227 (1), yet is wholly composed of cryptocrystalline quartz according to all microscopical, X-ray diffraction, and differential thermal data.

### Coarsely Crystalline Quartz

Typical fine- to coarse-grained quartz, either clear or milky, is not deleteriously reactive with cement alkalies. Typical expansion of moist-stored mortars containing high-alkali cement and quartzite or igneous quartz is in the range 0.01 to 0.04 percent at 1 year. It is interesting to note that the mortar bar data suggest that a low degree of reaction occurs in such specimens. If in a series of mortar bars a pure limestone or basalt is replaced progressively by crystalline quartz, expansion increases from possibly 0.01 to 0.03 percent at 1 year.

Conversely, convincing evidence has recently been obtained to demonstrate that coarsely crystalline quartz which is intensely fractured, strained, and granulated internally as the result of metamorphic processes during geologic time, or which is charged with microscopical or submicroscopical inclusions, can cause a deleterious degree of expansion of mortar or concrete containing a high-alkali cement. The expansion can be observed either in a procedure like ASTM Method C 227 (1) or like ASTM Method C 342 (1), or in exposed concrete in structures (6). Illite is common as inclusions in this type of quartz. The potentially deleteriously reactive quartz particles typically are white or milky; however, not all white or milky quartz is deleteriously alkali-reactive. The petrographic or mineralogical criteria by which potentially deleterious crystalline quartz can be distinguished from innocuous quartz remain to be developed.

The limited petrographic studies made so far on concrete adversely affected by alkali-aggregate reaction involving coarsely crystalline quartz suggest that potentially deleteriously reactive quartz must constitute the bulk of either the fine or the coarse aggregate before serious distress is manifested in the concrete in service.

### Tridymite and Cristobalite

Tridymite and cristobalite are recognizable by established mineralogic criteria and techniques. These minerals should be sought during the examination of volcanic rocks, tuffs, and fired siliceous products, such as high-temperature silica brick. Although these minerals typically constitute minor proportions of rocks, tridymite occasionally is highly concentrated, such as in a rhyolite tuff occurring near Castle Rock, Colo., and causes great expansion (over 0.400 percent at 1 year) in combination with high-alkali cements in procedures like ASTM Method C 227. These minerals probably should be considered to be potentially deleteriously reactive in amounts greater than 1 percent of the aggregate.

### Volcanic Glass and Devitrified Glass

Natural volcanic rocks and tuffs owe their alkali reactivity primarily to a matrix of siliceous glass and cryptocrystalline products of devitrification. Glasses with index of refraction less than 1.535 are known to be deleteriously alkali-reactive; glasses with index of refraction as high as 1.57 should be viewed with caution. Such glasses are typical of rhyolites, dacites, and andesites. Glasses whose index of refraction is in this range commonly occur in basalts as the result of deuteric (late volcanic stage) alteration; in this situation, tridymite and/or cristobalite commonly are abundant.

The cryptocrystalline devitrified phases of the acidic and intermediate volcanic rocks include matrices which are composed of masses of submicroscopical crystals producing a hazy birefringence between crossed nicol prisms, spherulitic growths, and granophyric intergrowths. These grade to the microcrystalline or fine-grained groundmasses, which are not deleteriously alkali-reactive.

Potentially deleteriously reactive volcanic rock almost always can be recognized with a hand lens or stereoscopic microscope by their vitreous, waxy, resinous, or satiny luster. Deleterious glassy or cryptocrystalline phases occur in obsidian, pitchstone, perlite, pumice, felsite, and the related porphyries and tuffs.

Aggregate containing 3 percent or more of rhyolite, dacite, latite, or andesite containing volcanic glass or cryptocrystalline phases should be considered to be potentially deleteriously alkali-reactive.

### Synthetic Siliceous Glasses

Synthetic siliceous glasses can be identified readily as a group by petrographic methods, but their composition must be determined by chemical analytical techniques. Only limited data are available on the potential deleteriousness of synthetic glass to portland cement concrete and mortar. The deleterious alkali reactivity of Pyrex has been proved in laboratory mortar tests; the expansion increases with the alkali content of the cement. Data are available also on the expansion of mortar bars prepared in a test like ASTM Method C 227 with an "opal" glass and a soft siliceous glass as aggregate. Not only were these glasses deleteriously reactive with high-alkali cement, but they also caused comparable expansion with a low-alkali cement, presumably because of release of alkalis from the glass itself in the alkaline environment of the hydrating cement. Siliceous glasses should be considered to be potentially deleteriously alkali-reactive in amounts as low as 1 percent.

## INFLUENCE OF FACTORS OTHER THAN LITHOLOGIC COMPOSITION ON ALKALI REACTIVITY OF AGGREGATE

### Availability of Alkalies from Aggregate

Alkalies (sodium and potassium) can be released from aggregate into mixing water or into solutions permeating cement paste of concrete in three general ways, as follows:

1. Alkali sulfates, chlorides, nitrates, or other water-soluble salts present in the aggregate may be dissolved both in the plastic and hardened concrete.

2. Alkalies can be released from certain minerals by cation exchange reaction with the calcic solutions in the concrete.

3. Alkalies in constituents of the aggregate may be released or their mode of combination may be changed by chemical reactions between these constituents and hydration products of the cement.

Water-soluble salts of sodium and potassium contribute to alkali-aggregate reaction in concrete or mortar roughly in proportion to the alkali concentration built up in the cement (7). Hence, if they are detected during petrographic examination, the concentration of water-soluble salts should be determined chemically. Water-soluble alkalies sufficient to produce a concentration in the cement paste equivalent to that produced in high-alkali cement justify rejection of an aggregate containing a deleterious proportion of alkali-reactive rock types and may preclude use of such aggregate in combination with other aggregates containing a deleterious proportion of alkali-reactive rock constituents.

Zeolites and clay minerals, especially montmorillonoids, can release sodium and potassium in sufficient amount to produce a high-alkali concentration in the cement paste. For concrete containing 1½-in. maximum-size aggregate, alkalies (as equivalents of soda) available by cation exchange reactions amount to about 0.15 percent by weight of the cement for each milliequivalent of exchangeable alkali per 100 grams of aggregate. Hence, even low levels of cation exchange capacity can be significant if potentially deleteriously reactive constituents are present. If calculation based on the results of chemical analysis indicates that a significant proportion of exchangeable alkalies is present in a coarse or fine aggregate, restrictions like those previously specified for aggregates containing water-soluble alkalies should be imposed.

With continued moist storage or exterior exposure of concrete, chemical reactions between the cement and aggregate will change the mode of combination of alkalies in rocks and minerals susceptible to attack by the alkaline solutions permeating the cement paste. As a result, progressively increasing proportions of alkalies may be rendered water-soluble according to a procedure in which the concrete is ground and leached by large excess of water. However, in spite of such an indication of increased availability, extensive data on cement-pozzolan reactions demonstrate that such alkalies typically do not participate in alkali-aggregate reaction (8). Apparently, alkalies which are water-soluble in a leach test of the type mentioned are not available for dissolution in the confines of mortar or concrete. In spite of the fact that these indications are derived from tests of pozzolans, there is little doubt that they may be applied to alkalies available from aggregate, because the active ingredients of natural pozzolans occur in aggregates and participate in the cement-aggregate reactions under discussion.

### Rock Texture

The internal texture and structure of a particle of aggregate influences in two ways the degree of deleterious activity produced in concrete by alkali-aggregate reaction. First, the extent of the chemical reaction is increased if the particle is sufficiently absorptive to permit the alkalies to penetrate into the interior of the particle. Second, the degree of distress effected in the mortar or concrete is reduced to the extent that the osmotic or swelling pressure resulting from the alkali-aggregate reaction is relieved by voids.

Hence, an optimum porosity and absorptivity will exist for most rock types. Opal or opaline cherts may be an exception to this generalization, inasmuch as the open molecular structure of opal permits sodium and potassium ions to penetrate rapidly by diffusion.

Among volcanic rocks, rhyolites, dacites, and andesites of moderate absorptivity and fracturing are more thoroughly attacked than are the dense, impermeable, vitreous particles. Highly porous volcanic types, such as some tuffs and pumice, produce little or no expansion of mortar even though the pores of the particles come to contain copious alkalic silica gel as the result of alkali-aggregate reaction.

Similarly, weathered, leached, and fractured chalcedonic and quartzose cherts and siliceous limestones participate extensively in alkali-aggregate reaction under some conditions and produce severe distress of concrete structures. Conversely, dense, unfractured cherts of similar type resist the progress of alkali-aggregate reaction and may be attacked only to the extent of a narrow reaction rim; in some instances such types have produced a serious degree of distress only after many years of service. Indeed, limited superficial reaction may be beneficial, rather than harmful, because of the improved bond between the aggregate and the cement paste.

### Particle Size

The expansion produced in concrete or mortar by alkali-aggregate reaction is influenced by the particle size of the deleteriously alkali-reactive particles in the aggregate (9). For highly reactive substances, such as opal, the degree of expansion increases with decrease of particle size at least to the No. 200-325 size range. Studies by Vivian (10) indicate that opal passing the No. 300 sieve is not deleteriously reactive; data published by Stanton (11) may be interpreted to the contrary. For slightly to moderately reactive deleterious substances, the degree of expansion increases with increase of particle size, at least to the No. 4-8 size fraction (9).

Data are lacking on this point for all but a few materials. However, it may be anticipated that such types as opaline chert and opaline limestones or dolomites will be quite deleteriously reactive, even in particles of fine sand. Conversely, aggregates containing chalcedonic and quartzose chert, chalcedonic and quartzose limestones and dolomites, siliceous phyllites, and siliceous slates would be expected to be more deleterious if these occur primarily in coarse sand and coarse aggregate.

### ESTIMATION OF POTENTIAL DELETERIOUS ALKALI REACTIVITY OF AGGREGATE BY PETROGRAPHIC EXAMINATION

The potential deleterious alkali reactivity of a sample of concrete aggregate can be determined qualitatively in two general ways by petrographic examination. First, by petrographic analysis the presence and frequency of potentially deleteriously reactive particles can be established with any desired accuracy. Second, by petrographic examination the aggregate can be compared in detail with other aggregates for which service records or test data are available.

If the necessary background data are available, comparison of the aggregate with others of similar lithology is the best way to establish the probable performance of the material. Provided the petrographic examination and analysis of the aggregates involved have been performed competently and in adequate detail, this method is more satisfactory than additional laboratory tests because the field service data are more reliable than laboratory tests. If only data from previous tests are available, the petrographic evaluation permits a quick determination and avoids the necessity for the expense of additional tests.

The reliability of the comparison depends, of course, on the lithologic similarity of the aggregates involved and the degree to which the anticipated service conditions match those of the concrete studied in connection with the review of the service records. Nevertheless, the procedure can be applied effectively over large areas in which comparable aggregates are supplied from deposits along major streams, deposits of continental glaciers, marine shoreline deposits, and geologic formations of wide distribution. For example, deposits of sand and gravel along the South Fork of the Loup River, lower Platte River, and the Republican River in Nebraska and Kansas can be compared petrographically and their performance evaluated in the light of their general performance.

Petrographic examination in accordance with ASTM Recommended Practice C295 (1) will reveal even minute quantities of potentially deleteriously reactive substances. Frequently, the proportion of such particles is below the limit considered to be significant. Less commonly, the proportion of the reactive particles is sufficiently high to suggest that no deleterious effects will occur because the ratio of reactive siliceous material to available cement alkalis is sufficiently high to produce a nonexpanding alkali-silica

combination. In some instances, the particles may be sufficiently dense and impervious, sufficiently fine in particle size, or sufficiently porous to be relatively innocuous even though they may be abundant enough to cause deleterious effects under other circumstances.

Hence, the petrographer is faced with a series of problems in the evaluation of potential alkali-aggregate reaction from results of the petrographic examination as follows:

1. What are the potentially deleterious substances?
2. How abundant are the potentially deleterious particles?
3. Are the potentially deleterious particles sufficiently abundant to require the limitations on the use of the aggregate?
4. Are there properties, such as alkalis available from the aggregate, excessive porosity, or range of particle size, which will modify the decision with respect to the anticipated degree of alkali reactivity and the justification for use of the aggregate with low-alkali cement?

In the petrographic laboratory of the Bureau of Reclamation limiting values have been placed on the various potentially deleteriously reactive rocks and minerals, as given in Table 2.

TABLE 2  
LIMITING VALUES ON POTENTIALLY REACTIVE ROCKS AND MINERALS,  
AS ESTABLISHED BY PETROGRAPHIC LABORATORY,  
U. S. BUREAU OF RECLAMATION

Rock Type	Maximum Content Permitted <sup>a</sup>
Opal and opaline chert	0.25
Chalcedonic or quartzose chert	5
Glassy to cryptocrystalline rhyolites, dacites, latites, or andesites and their tuffs	3

<sup>a</sup>Unless use of low-alkali cement is recommended.

The permissible percentage of rock types containing smaller proportions of the deleterious phases is increased roughly in inverse proportion to the amount of the deleterious phase present.

Experience has demonstrated that these limiting values are conservative. Review of data comprising petrographic analyses over several years in the Bureau's petrographic laboratory demonstrates that an indicated innocuous character for an aggregate is virtually always confirmed if tests of mortar subsequently are made in accordance with a procedure similar to ASTM Method C 227. Conversely, an indicated deleterious degree of potential alkali reactivity frequently is not corroborated by the standard mortar expansion test. However, it is not concluded from such a finding that the indication of the petrographic examination is in error. For example, excessive expansion may not be obtained because insufficient time is allowed in the test, a deleterious ratio of reactive siliceous material to available alkalis may not be established in the test mortar whereas it may be in the concrete in the field, or variations of temperature and moisture content incident to natural exposure might induce alkali-aggregate reaction to a degree not demonstrated by the moist-stored mortar tests.

Ordinarily, the probable effects of alkalis available from the aggregate and of absorptivity, particle size, and internal porosity of the aggregate are insufficient to justify modification of the indicated limits and recommendations on use of the aggregate. However, such factors should be kept in mind during petrographic examination of concrete as a means to establish alkali reactivity of the aggregate. In two instances from a total of several hundred aggregates, limitations were placed on use of aggregate because of availability of exchangeable alkalis. In one, a coarse aggregate was approved for use only with fine aggregates which are not deleteriously alkali-reactive. In the

other, the source was rejected because the aggregate itself was potentially deleteriously alkali-reactive so that specification of low-alkali cement would be to no avail. For lightweight aggregate, the high porosity frequently will produce an innocuous character, even in the face of high chemical reactivity.

In spite of the apparent vagaries involved in interpretation of the petrographic examination, experience in the Bureau of Reclamation laboratories has led to abandonment of the moist-stored mortar test as a routine method to evaluate potential alkali reactivity of aggregate in favor of petrographic examination. The mortar test is performed only for those aggregates whose marginal reactivity or content of rocks upon which inadequate data are available precludes satisfactory evaluation by the petrographic examination.

### CONCLUSIONS

1. Petrographic examination in accordance with ASTM Recommended Practice C 295 is a dependable means to evaluate the potential deleterious alkali reactivity of aggregate for concrete.
2. Validity of the results depends on the training, experience, and diligence of the petrographer. However, with proper training and adoption of uniform techniques and nomenclature, subjective elements in the examination are not significant.
3. Conclusions concerning potential alkali reactivity based on petrographic examination are likely to be conservative because even trace amounts of potentially deleterious substances can be detected. Unrealistic conclusions concerning potential alkali-aggregate reactivity can be avoided by application of the maximum permissible limits for various rocks and minerals recommended in the text of these remarks.
4. Research should be continued to elucidate the deleterious alkali reactivity of rocks and minerals for which existing data and experience are inadequate.

### REFERENCES

1. Amer. Soc. for Testing Materials, "ASTM Book of Standards." Part 3 (1956).
2. Mielenz, R.C., "Petrographic Examination of Concrete Aggregate." Proc., ASTM, 54:1188 (1954).
3. Stanton, T.E., "Expansion of Concrete Through Reaction Between Cement and Aggregate." Trans., ASCE, 107:54 (1942).
4. Eitel, W., "The Physical Chemistry of the Silicates." Univ. of Chicago Press (1954).
5. Mather, B., "Petrographic Identification of Reactive Constituents in Concrete Aggregate." Proc., ASTM, 48:1120 (1948).
6. Brown, L.S., "Some Observations on the Mechanics of Alkali-Aggregate Reaction." ASTM Bulletin, No. 205, 40 (1955).
7. Kelly, T.M., Schuman, L., and Hornibrook, F.B., "A Study of Alkali-Aggregate Reactivity by Means of Mortar Bar Expansion." Proc. Amer. Conc. Inst., 45:57 (1948).
8. Mielenz, R.C., Ramaley, D., Benton, E.J., and Geier, F.H., "Pozzolans and Cement-Pozzolan Reactions." Bureau of Reclamation, Petrographic Lab., Report No. Pet-102, 25 pp. (1952).
9. McConnel, D., Mielenz, R.C., Holland, W.Y., and Greene, K.T., "Cement-Aggregate Reaction in Concrete." Proc. Amer. Conc. Inst., 44:93 (1947).
10. Vivian, H.E., "Studies in Cement-Aggregate Reaction: XIX. Effect on Mortar Expansion of the Particle Size of the Reactive Component in the Aggregate." Australian Jour. Appl. Sci., 2:488 (1951).
11. Stanton, T.E., "Studies of Use of Pozzolans for Counteracting Excessive Concrete Expansion Resulting from Reaction Between Aggregates and the Alkalies in Cement." ASTM Spec. Tech. Publ. No. 99, 179 (1949).

### *Discussion*

KATHERINE MATHER, Waterways Experiment Station, Corps of Engineers, Jackson, Miss. —Because alkali-aggregate reaction is frequently complex in its field manifesta-

tions, and because regional differences in the composition of aggregates and in the climatic exposure cause the manifestations to differ in different parts of the country, it is not surprising that experience suggests some shifts in emphasis and some alternative interpretations.

#### Lower and Upper Limits on Chert Content

The author has suggested lower limits of content of several reactive substances, above which content the aggregate may be considered potentially deleteriously reactive. In Mississippi and eastern Louisiana, at least, upper limits are needed as well; values above which the pessimum proportion is so far surpassed that the aggregate is safe to use. All of the gravels of this area contain 80 to 95 percent chert. If the indexes of refraction have not been raised by iron oxide stain, search will reveal more or less chert with aggregate indexes of refraction below 1.544, the lower refractive index of low quartz.

Chert with refractive index below this value is regarded as chalcedony. All of these gravels come out deleterious in the quick chemical test; many develop gel in the mortar-bar test; none have expanded as much as 0.1 percent at one year in the mortar-bar test. The sands occurring with the gravels contain about 5 to 15 percent chert, increasing as the sizes retained on No. 30 sieve increase. Some of the chert is chalcedonic by the foregoing criteria. More evidence of reaction appears in the sand-mortar bars than in those containing the gravel.

These materials have been used in many structures, for they are the only locally available aggregates except for lightweight aggregates. As far as is known there is no demonstrated case of deleterious cement-aggregate reaction. Many specimens of concrete from structures built with these aggregates have been examined, and microscopic evidence that reaction has taken place has been found. However, no evidence has been found of expansion or displacement. Reaction appears to be so general that concrete more than a year or so old breaks through rather than around the smooth-surfaced chert coarse aggregate.

To the east, in Alabama, the proportion of chert in the gravels decreases. The coarse aggregate in the Tuscaloosa Lock cores examined at the Waterways Experiment Station contained 40 percent chert and 60 percent quartz, quartzite, and sandstone. The lock structure does show deleterious cement-aggregate reaction. In concrete made with these aggregates, the division between safe and unsafe chert content of gravel appears to lie somewhere between 40 and 85 percent. Less information is available about the sand. In mortar-bar tests of similar materials, more expansion has developed with sands containing 4 or 5 percent chert, including some chalcedony, than with sands of higher chert and chalcedony content.

#### The Silica Minerals and Mineraloids

There is general agreement that opal, tridymite, cristobalite, and high-silica volcanic glass are reactive, and there is general agreement on how to identify them. There is an increasing degree of agreement that chalcedony is reactive, and the trend appears to be toward identifying chalcedony as cryptocrystalline and microcrystalline silica with an aggregate index of refraction below the lower index of low-temperature quartz (1.544). This criterion is satisfactory in many cases, but does not serve for iron-stained chalcedony, where the stain raises the index of refraction into the quartz range.

Examples have been found in the laboratory of development of gel on bars presumably made with a crushed sedimentary quartzite, which in all the samples examined had contained only traces of constituents other than quartz. Because the presence of the gel was surprising, the mortar beneath the gel spots was dissected under the microscope; under every gel spot was found either a particle of pyrex or a particle of opal, accidental contaminants in the bars.

Dr. Mielenz discusses instances, including one cited by Brown, of structures showing alkali-aggregate reaction in which the predominant constituent of the aggregate is highly metamorphic quartz. Apparently all of these involve the Long Island aggregates

or closely similar aggregates. A petrographic examination of a Long Island gravel showed 3 percent chert; the analysis was made in 1941, before determination of index of refraction of chert became standard practice. Recently, examination of three test specimens containing Long Island gravel and sand that had been exposed at St. Augustine since the Fall of 1940 was begun. The coarse aggregate in all three contains some chert; indexes of refraction have not yet been determined. One column was made with a high- $C_3A$  cement with an alkali content of 1.08 percent expressed as  $Na_2O$ ; the concrete contains a great deal of calcium sulfoaluminate and considerable alkali-reaction gel. Some of this gel is associated with dark-red clinker or glassy slag present as a contaminant in the coarse aggregate.

In summary, the writer feels that it has not been demonstrated satisfactorily that microcrystalline or cryptocrystalline or coarsely crystalline quartz needs to be regarded as reactive at the temperatures and alkali concentrations found in concrete exposed in structures.

**LEVI S. BROWN, Portland Cement Association**—The introduction given by Dr. Mielenz has been so inclusive in scope, history, and findings that little in the way of objective information remains to be offered. It may be worthwhile, however, to venture some remarks of a descriptive or qualitative interest.

To begin with, the efficacy or advantage of the petrographic approach depends upon a prior knowledge. The author has presented an inclusive outline of rocks and minerals that in one way or another have been found vulnerable to alkali attack. To decide upon potential alkali reactivity of a proposed new aggregate, it is only necessary to examine the new material to see if any of the known reactive rocks or minerals are present. There is no particular trick to this operation. It is simply a matter of piece-by-piece examination and count classification according to substance identification, with or without magnification as may be required. Numbers make the operation perhaps a bit tedious, but the whole operation is vastly faster than any bulk or empirical test.

The list of known reactive materials has been compiled from essentially three sources. Stanton first provided a basic insight into vulnerable siliceous substances with his published recognition of alkali-aggregate reaction. Secondly, the list has been augmented by results from certain chemical tests and mortar bar tests, devised for the purpose, and supplemented by petrographic description of the substances tested. Thirdly, much has been learned from study of distressed field structures, as such have come to notice. In these instances it was not a matter of advance notice or suspicion or selection of the aggregate. It was only a matter of recognition of a substance as having reacted, whether or not priorly known to be reactive. Others may become known from future examinations.

In this latter connection the author offers opportunity for further comment, in speaking of alkali-aggregate reaction as a phenomenon separable from other processes by which concrete deteriorates. The meaning, of course, is that alkali-aggregate reaction is an agent which is within itself a source of potentially damaging force.

But in visual examination of deteriorated concretes or distressed structures, alkali-aggregate reaction, if present, is not always easily separable from other damaging agents in the sense of recognition as the prime or essential offender. It is one thing to perceive evidence of chemical alteration of some pieces of aggregate; it is something else to perceive evidence that the chemical alteration has been instrumental in the deterioration of the concrete or in the distress of the structure, or even to trace the latter effects to action of other agents. For example, field investigations have turned up some structures wherein alkali-aggregate reaction was prominently present but without discoverable disturbance of either strength or continuity of the concrete. In fact, the distress obviously was introduced by some other agent.

There have been field occurrences, also, wherein the same cement and the same aggregate have been used in the same project, with the surprising fact that parts of the project showed prominent reaction and extensive damage therefrom, whereas other parts of the project were perfect and showed no indication of reaction. There have been cases of severe distress with one high-alkali cement, but perfect performance with a cement



even higher in alkalis although combined with the same aggregate. There have been other cases where the concrete was obviously deteriorated and no specific cause could be perceived, although there was good reason to suspect alkali-aggregate reaction.

These observations suggest that damage or deterioration of concrete by alkali-aggregate reaction is not a matter solely of compatibility of components, as might be inferred from a simple listing of rocks and minerals found to be reactive. Deleterious effects evidently are dependent in some measure upon conditional features, which are not always clearly perceived. This is not particularly new; Stanton in his initial papers showed the influence of particle size and of proportion of reactive material in the aggregate. The latter observations have become the basis for the so-called pozzolanic protection, now relatively well-known.

Adequate preventive measures obviously require adequate recognition of deleterious processes. Recognition of reactive substances by petrographic techniques is relatively easy. There is some prospect that conditional features may be resolvable by petrographic means, but these offer far more difficult problems. Despite manifold uncertainties, notable progress has been made, under pressure of time, by several large builder organizations.

# Performance of Tests for Cement-Aggregate Reaction

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●DURING the investigation of cases of excessive expansion in concrete in Canada by the Division of Building Research, certain results were obtained which may be of interest in appraisal of the methods of test for alkali-aggregate reaction. The scope of this work covered the quick chemical and mortar bar tests carried out in this laboratory, final petrographic evaluation by recognized authorities in the United States, and other special tests.

## Case I

Petrographic evaluation of a deteriorated concrete slab and of aggregate samples from the original sources revealed unmistakable evidence of alkali-aggregate reaction: fractures, secondary chemical deposits, alkalic silica gel, reaction rims, and pattern cracking resulting from excessive expansion. A high-alkali cement had been used. The rate of expansion in the field cases was very slow.

The reactive components in the crushed boulders and the coarse fraction of the sand were phyllites and smaller amounts of chalcedonic sandstone, meta-sandstone, and chalcedonic limestone.

The quick chemical test (ASTM C289-54T) gave values of reduction of alkalinity and silica release well within the region of deleteriously reactive aggregate, as proposed by Mielenz, Greene and Benton (1).

The standard mortar bar test (ASTM C227-52T) gave negative results for both stone and sand materials as obtained from the original sources.

Because the proportion of deleterious materials in these samples may have differed from those in the field cases, a repeat series was tested in which dilutions were made. To date, at ages up to nine months, the expansion in these mortar bars shows no indication of approaching the critical limits.

The Conrow test (ASTM C342-55T) also gave negative results for these materials. The accelerated reactivity test on concrete beams, the method originally proposed by the Bureau of Reclamation, was also negative. A wetting and drying test on concrete beams (similar to the Scholer method) produced excessive expansion on beams made from these materials, but had similar effects on beams made from known unreactive materials.

## Case II

Concrete sidewalks, floor slabs, and other concrete elements exposed to high humidity conditions showed excessive expansion accompanied by map cracking. Preliminary tests indicated that a crushed limestone aggregate was the cause of the trouble. A high-alkali cement had been used in this case also. The rates of expansion in the field concrete and in the laboratory concrete beams exposed to 100 percent relative humidity conditions were very rapid, being in the order of 0.1 percent in three months and 0.2 percent in six months.

Opinions expressed by independent authorities in the field, who had made careful analyses, agreed that alkali-aggregate reaction was the cause. An unusual feature of this case was that gel formation, usually associated with this reaction, was almost non-existent. The degree of definition of reaction gel rims was a matter of minor disagreement, and the nature of the reactive component was somewhat uncertain.

The quick chemical test gave negative but rather unusual results, with a very high reduction in alkalinity and a low silica release. According to Mielenz, Greene and Benton (1), these results should indicate a very safe material as far as alkali-aggregate reaction is concerned. Mortar bar test results, as far as they have now progressed,

may be considered as borderline. The expansion at six months ranged from 0.025 to 0.045 percent.

Replacement of 25 percent of the high-alkali cement by a pozzolanic material had the positive effect of considerably reducing the expansion. The low-alkali cement had the same effect. Concrete beams made with crushed limestone as coarse aggregate expanded rapidly under conditions of: (a) outside exposure, (b) exposure to wetting and drying, and (c) exposure to 100 percent relative humidity at 23 C.

The possibility that the "pessimum" was missed has prompted further work on "diluted" materials, particularly since this case appears to be the type where optimum expansion occurs with a low percentage of deleterious material. To date no conclusive results have been obtained.

The Conrow test on this material was negative.

### Tentative Conclusions

1. In Case I, all evidence indicates alkali-aggregate reaction except the results of the mortar bar test. It appears to be similar in nature to the reaction occurring in the Buck Hydroelectric Dam, and represents a type which, reportedly, is not too well understood. Pending further study, it would seem necessary to clarify the status of C227-52T by correcting the impression that the mortar bar test is the most reliable of the three procedures for detecting cases of alkali-aggregate reaction, and providing an explanatory note in C227-52T with suggestions for the blending of materials in order to ensure that the proportions of deleterious materials will include the expansive combination.

2. Case II is apparently a very unusual type of alkali-aggregate reaction in which the quick chemical test fails and the mortar bar test is borderline. In view of the results obtained, alkali reactivity in limestones should be re-examined in order to determine more precisely the differences that exist in their response to present test methods as compared with siliceous aggregates. This applies particularly to the quick chemical method. The effect of carbonates on the reduction of alkalinity warrants study. It would also seem logical that a suitable factor should be used in calculating silica release from limestones which would be dependent on the total amount of silica material present in the aggregate.

The borderline nature of the mortar bar test results in Case II, and the very rapid expansion of concrete specimens, seem to indicate the need for extending C227-52T to include blends for the mortar bar test and the exposure of companion concrete samples to selected conditions. The reduction of stone size to sand size for the mortar bar test may, in this case, have reduced the expansive tendency of the mortar in accordance with recent theories.

### REFERENCES

1. Mielenz, R. C., Greene, K. T., and Benton, E. J., "Chemical Test for the Reactivity of Aggregates with Cement Alkalies: Chemical Processes in Cement-Aggregate Reaction." Proc., Amer. Conc. Inst., 44:193 (1947).

# General Discussion of Test Interpretation

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● THIS discussion describes an instance in which laboratory tests were made on samples representing two sands considered for use on the same project. Both of these sands were natural river sands and, as produced, were deficient in material in the finer sizes. A fine sand from a third source was used to correct grading deficiencies in both. Preliminary data on the sands are given in Table 1. The petrographic examination revealed that both sands consisted of essentially unweathered materials, and that their constituents were similar.

TABLE 1  
CHARACTERISTICS OF TWO NATURAL RIVER SANDS

Item	Sand A	Sand B
Source	Miss. R.	Ohio R.
Blending sand used (%)	6	11
Absorption (%)	0.5	1.3
Soundness <sup>a</sup> (%)	3.2	3.6
Coal and lignite (%)	0.1	0.4
Comp. stress ratio (%):		
3-day	102	103
7-day	101	113
Cumulative percent passing:		
$\frac{3}{8}$ in.	100	100
No. 4	98	95
No. 8	90	85
No. 16	74	73
No. 30	50	51
No. 50	16	17
No. 100	4	5
No. 200	0.8	1.4
Fineness modulus	2.68	2.75
Specific gravity	2.63	2.59
DFE <sub>300</sub> with C.A. "C"	48	43
DFE <sub>300</sub> with C.A. "D"	49	43

<sup>a</sup>Loss after 5 cycles of magnesium sulfate.

The weighted average composition was found to be as follows:

	Sand A	Sand B
Quartz	65	56
Feldspar	18	8
Chert	5	19
Igneous rocks	8	6
Sandstone	—	9
Miscellaneous	4	2
Total	100	100

dense, brown, rounded and smooth. Some of the chert in each sample is chalcedonic, but it is believed that not more than one-half of the chert in either sample is chalcedony. More detailed estimates of chalcedony content were not made because word was received from the field that a decision to require low-alkali cement had already been made on the basis of previous work and service records.

The quartz grains are mostly clear and clean. The feldspar grains are mostly fresh and blocky. The igneous rock particles are mostly coarse-grained granite, but include a very minor amount of dense dark rocks. The sandstone particles are fine-grained. The miscellaneous group includes wood, coal, charcoal, coke, slag, flyash, carbonate rocks and minerals, sandstone (in A), organic debris, mica flakes, clay pellets, and undifferentiated materials. Most of the chert grains are

The distribution of chert by sieve sizes is given in Table 2.

TABLE 2  
PRELIMINARY DISTRIBUTION OF  
CHERT BY SIEVE SIZE

Sieve Fraction	Chert (%)	
	Sand A	Sand B
+ No. 4	—	61
No. 4 - No. 8	17	55
No. 8 - No. 16	7	41
No. 16 - No. 30	2	11
No. 30 - No. 50	2	2
No. 50 - No. 100	8	1
No. 100 - No. 200	5	2
Weighted Average	5	19

The larger amount of chert, especially in the coarser sizes, in sand B, was regarded as probably explaining the higher absorption of sand B and the lower durability factor of concrete made with it, as compared to sand A.

The results of the quick chemical test were:

	Sand A	Sand B
$S_c$ , mM/1	150	84
$R_c$ , mM/1	89	61

Both of these pairs of values give points in the "deleterious" area of the  $S_c/R_c$  plot; however, the point for sand A is three times as far from the dividing line as the point for sand B.

In the discussion of the test results made at this stage in the investigation, it was noted that:

1. Sand B contained more chert and gave concrete of slightly less resistance to freezing and thawing.
2. Sand A appeared slightly more deleteriously reactive by the quick chemical test.

For use in the mortar bar test, mixtures were prepared consisting of 94 percent of sand A plus 6 percent of blending sand and 89 percent of sand B plus 11 percent of blending sand. The mixtures were separated into individual sieve fractions and recombined to the specified grading as given by CRD-C 123 for the mortar bars. The chert content of the sieve fractions of the blended sands and the weighted average chert content of the blends in the mortar bar grading are given in Table 3.

TABLE 3  
CHERT CONTENT OF SIEVE FRACTIONS OF BLENDED SANDS AND WEIGHTED  
AVERAGE CHERT CONTENT OF BLENDS IN MORTAR BAR GRADINGS

Sieve Retained On	Sand A (94 + 6%)		Sand B (89 + 11%)	
	Chert (%)	Wtd. Ave. Chert (%)	Chert (%)	Wtd. Ave. Chert (%)
No. 4	23.5	0.59	54.3	1.36
No. 8	16.0	1.20	49.0	3.67
No. 16	6.6	0.66	36.5	3.65
No. 30	1.9	0.66	9.8	3.43
No. 50	2.2	0.67	2.3	0.70
No. 100	7.8	0.86	1.4	0.15
No. 200	4.9	0.17	2.1	0.07
- 200	0.1		0.1	
Total	—	4.81	—	13.03

It was the petrographer's speculation that sand A would show more expansion in mortar bars. This speculation was based on the observation that most mortar bars made with natural sand, tested in this laboratory, that had shown excessive expansion in which chalcedonic chert was the reactive constituent, had contained approximately 5 percent chert.<sup>1</sup>

<sup>1</sup>See Katherine Mather's discussion of "Petrographic Examination of Concrete Aggregate to Determine Potential Alkali Reactivity." p. 35.

When the mortar bars were six months old, it was apparent that little expansion was taking place with either sand and low-alkali (0.37 percent  $\text{Na}_2\text{O}$  equivalent) cement and only minor expansion with sand B and high-alkali (0.95 percent  $\text{Na}_2\text{O}$  equivalent) cement, but the expansion of bars with sand A and high-alkali cement had exceeded 0.05 percent. The results at one year were:

	Expansion (%)	
	Sand A	Sand B
Low alkali	0.013	0.013
High alkali	0.136	0.024

TABLE 4

## EXPANSION OF MORTAR BARS, PERCENT

Sand A		Sand B	
High-Alkali Cement	Low-Alkali Cement	High-Alkali Cement	Low-Alkali Cement
0.103	0.012	0.029	0.013
0.112	Broken	0.026	0.016
0.104	0.013	0.029	0.016
0.130	0.013	0.024	0.012
0.160	0.009	0.022	0.012
0.168	0.013	0.020	0.011
0.128	0.013	0.023	0.011
0.169	Broken	0.021	0.012
0.150	0.015	0.026	0.013
0.136 <sup>a</sup>	0.013 <sup>a</sup>	0.024 <sup>a</sup>	0.013 <sup>a</sup>

<sup>a</sup> Average.

The agreement among the mortar bars included in these averages is quite good, as indicated by the individual values (Table 4). The results of petrographic examination of the 36 mortar bars after termination of the mortar bar test at one year are shown in Table 5. The brown spots consisted of a tarry material believed to represent decomposition of coal and lignite particles in the aggregate. Only the bars that showed excessive expansion showed cracking; these bars also showed more gel both on their surfaces and in their interior, and were so weak as to be easily broken by hand.

The reasons why the abnormal expansion should have occurred with the sand of lower chert content and not with the sand of higher chert content remain to be positively established. The difference is in the direction indicated by the quick chemical results and by the speculations of the petrographer. The magnitude of the difference is greater than would have been suggested by the magnitude of the differences in the quick chemical test results.

The petrographer has observed that, although the difference in mortar bar results may be due to differences in composition or constitution (chalcedony and/or opal content or pore structure), no such differences were detected in the petrographic examination and hence such differences did not influence the speculations. It may be that the fact that Sand A has 8 percent chert in the No. 50 to No. 100 size while sand B has only 1 percent in this size, or that sand B with 13 percent chert was on the high side of the "pessimum" content, or both, is responsible for the results obtained in the mortar bar tests.

This example suggests that the results of petrographic examination should, at least in some cases, be taken primarily to indicate the presence or absence of potentially deleterious constituents in the sample examined rather than to indicate the degree of reactivity to be expected of samples that have appreciable but differing quantities of such constituents.

In the present case, the two sands were both classed as deleterious by the quick

TABLE 5  
RESULTS OF PETROGRAPHIC EXAMINATION OF MORTAR BARS  
AFTER TERMINATION OF TEST

Item	High-Alkali Cement <sup>a</sup>		Low-Alkali Cement <sup>b</sup>	
	Sand A	Sand B	Sand A	Sand B
Water content (ml)	230	238	230	238
Expansion, 1 yr (%)	0.136	0.024	0.013	0.013
Warping	None	None	None	None
Cracking	Scattered short, few deep	None	None	None
Surface condition	Gel spots Brown spots	Few gel spots Brown spots	Brown spots	Brown spots, more than with sand A
Sulfoaluminate	None	None	None	None
Gel	Many spots on surface; one gel-filled void, few voids with gel lining	Few spots on surface; few voids with thin gel lining	Very few small spots on surface; no gel in voids	Very few small spots on surface; no gel voids
Strength	Bars weak	Bars strong	Bars strong	Bars strong

<sup>a</sup> RC-167.  
<sup>b</sup> RC-168.

chemical test; potentially deleteriously reactive constituents were detected in both by petrographic examination; one showed definitely abnormal expansion (0.136 percent) in high-alkali cement mortar bars, while the other showed only slight expansion (0.024 percent).

It is not known which sand, if either, has been selected for the project; but it is believed that if either sand is used, the decision to require low-alkali cement was proper.

## ***Part III***

### ***Theoretical Considerations***



# A Review of Fundamental Research on the Alkali-Aggregate Reaction

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● EXTENSIVE research conducted in the past decade on the alkali-aggregate reaction has shown the problem to be extremely complex and all the intricate relations have not as yet been fully established.

The consecutive developments which produce the expansion resulting from this reaction may be summarized as follows:

The sodium and potassium hydroxides present in the free water of the concrete as a result of the cement hydration react with certain types of siliceous minerals contained in the aggregate. This reaction produces a semi-solid gelatinous material, commonly referred to as an alkali-silicate gel, which has a tendency to absorb water and solution. When the gel is confined by the rigid cement paste, the natural tendency to increase in volume as a result of the absorption of liquid creates internal pressures within the concrete. When these internal pressures are of sufficient magnitude to exceed the tensile strength of the mortar, cracking and expansion occur.

Generally, results of research investigations to date have shown that the detrimental effects from this reaction cannot be simply equated to either the amount of alkali or the amount of reactive material present. The over-all effect results from a combination of factors, which include, among others, availability of alkali and water, particle size of the reactive portion of the aggregate, temperature and moisture conditions during the curing and service of the concrete, the ratio of alkali to reactive silica present, and the permeability of the cement paste.

It is the chemical and physical properties of the alkali-silicate gel and the manner of its formation which make the over-all problem of the alkali-aggregate reaction very complex. Usually when two inorganic substances react, definite amounts of each material combine to form a specific product. In such a reaction, any excess of one reactant over the other would not alter the properties of the product produced. However, this is not true of the reaction between alkali hydroxide and silica. In this case, the product is a gel system in which the alkali and silica are combined in a number of different ways. Both the amount and the properties of the gel product formed depend in part on the relative amount of each original constituent present. In addition, the gel originally formed is not stable but changes depending on the surrounding conditions and on the amount of solution and water absorbed.

Thus, the gel present in concrete under some conditions may be solid or semi-solid and capable of exerting considerable pressure as a result of its absorptive properties. Under other circumstances it may be present as a fluid and would diffuse out of its confined area or be forced out with only moderate pressures that may not be sufficient to damage the surrounding matrix. In other instances, calcium hydroxide may enter into the gel formation, resulting in a non-absorptive product that does not produce internal stresses.

The following discussion attempts to summarize the more important developments relating to various phases of the problem. These are described generally in the order in which they occur in the concrete.

## THE INITIAL CHEMICAL REACTIONS

### Source of Alkalies

As portland cement hydrates, the alkali constituents in the cement dissolve. Complete solution of the alkalies has been variously reported to occur within 1 month (1, 2) and 3 months (3). The alkalies appear in the solution surrounding the cement paste as alkali hydroxides (that is, sodium and potassium hydroxide), and are then free to attack reactive aggregates present in the concrete. The alkali hydroxides may also be

derived from alkali-containing zeolitic minerals if these are present in the aggregate as a result of a reaction in which the lime from the cement displaces the alkali from the zeolites (4). In most cases, however, the alkalis are derived from the cement (5).

### Reactive Aggregate

Deleteriously alkali-reactive aggregates usually are those containing opal, chalcedonic silica, or certain glassy or very fine-grained volcanic rocks. Some consideration has been given to the chemical and physico-chemical nature of opal (5, 6). Powers and Steinour give a rather informative description of the nature of the reactive particle (5). They suggest that opal can be considered a highly condensed silica gel. They further explain that such a material, by virtue of its genesis, contains a large surface area (mainly, internal surface area). Because of the existence of broken silicon-to-oxygen bonds at any surface of silica, and therefore uneven charges, surface hydration occurs. Consequently, both the internal and external surface of opal may be considered to be a hydrated surface. However, the water attached to the silica surface consists of hydrogen ions ( $H^+$ ) and hydroxyl ions ( $OH^-$ ), which are attached to the oxygen and silicon atoms, respectively.

Because the hydrogen ions are bound less firmly than are the hydroxyl groups, ionization occurs in aqueous media to free some of the hydrogen ions. Consequently, the surface of the silica particle contains an excess of ionized hydrogen ions and is therefore weakly acidic. Since opal and similar reactive particles contain large internal surface areas, they represent an extremely large surface possessing acidic properties.

### Initial Chemical Reaction

As a consequence of the acidic surface properties of the reactive silica particle, the initial reaction with an alkali hydroxide (such as sodium hydroxide) is considered by Powers and Steinour (5) to be an acid-base neutralization. The surface hydrogen ion unites with the hydroxyl ion from sodium hydroxide, forming free water, while the sodium ion attaches itself to the negatively charged surface-oxygen atom. Pike and Hubbard (7), approaching this problem from a different point of view, arrived at essentially the same conclusion. They consider the surface of the reactive silica particle to behave as negatively charged non-migratable ions, presumably by assuming the removal of the weakly attached hydrogen ions ( $H^+$ ). Consequently, the surface offers some attraction for positive ions, such as sodium ( $Na^+$ ). Vivian (8) emphasizes that the hydroxyl ion is of considerable importance in any attack on opal and similar materials. He showed considerable attack upon opal, using alkaline materials such as tetramethylammonium hydroxide.

Powers and Steinour (5) suggest that as the process of the neutralization reaction continues, additional alkali invades the reactive particle, and the silica gel becomes more and more peptized, the particles of colloidal silica thus produced becoming smaller. This action is accompanied by an invasion of water which produces swelling. Hurd and Laning (9) give an interesting mechanism to explain why such a reaction may continue. They suggest that in the reaction between sodium hydroxide and silica gel, the sodium hydroxide first neutralizes the simpler silicic acids at the surface of the silica as these acids are stronger than the highly condensed poly-acids below the surface. This neutralization of the simpler species upsets the equilibrium and causes an adjacent inner layer of more highly condensed polysilicic acids to hydrate to simpler acids. These in turn are neutralized by the sodium hydroxide. This cycle continues until the particle is completely attacked.

Hansen (10) has shown that the deleterious end product of the reaction (an alkali-silica complex) can normally occur in concrete as an apparent solid, or gel, or simply a solution. This is explained by the fact that when the available water in concrete is scarce and/or the alkali concentration is limited, the reaction will be limited, resulting in a solid product (5). If more water and/or alkalis are available, the reaction proceeds to a greater extent, producing a gel-like product. Ultimate reaction would, of course, produce a solution. As a consequence, the ratio of alkali to silica in the reaction product increases as the attack progresses, so that reaction products vary over a considerable range with respect to their alkali-to-silica ratio.

## Expansion

The newly formed reaction product has a tendency to imbibe water (or cement paste solution) and increase in volume. Because the reaction product is confined by the comparatively rigid cement paste, this tendency of the reaction product to increase in volume creates internal pressures within the concrete. When such pressures are of sufficient magnitude to exceed the tensile strength of the surrounding cement paste, cracking and ultimate expansion of the concrete occur. Pile et al. (11) have shown that the volume of opal may increase 300 percent while being transformed to the final reaction product.

As previously stated, the detrimental physical effects of this reaction in concrete depend on a combination of several factors, such as availability of alkali and solution; porosity of cement paste (12); nature, size, and distribution of reactive constituents; and temperature of the concrete. For example, Vivian demonstrated that rigid reaction gels became mobile when heated to 109 F or more. These gels became viscous again when cooled. He suggests that this may explain why decreased expansion occurred in mortar bars at elevated temperatures (13).

## Effect of Calcium Hydroxide

The existence of an alkali-silica reaction product in concrete is contradictory to what might be expected, because of the presence of sufficient calcium hydroxide in cement paste to form a non-expanding lime-alkali-silica product. Powers and Steinour (5, 14) speculate that the alkali-silica complex is able to persist because of the inability of the lime to diffuse to the reaction site at a sufficiently high rate. They suggest that the initial reaction produces a thin layer of lime-alkali-silica complex at the surface of the reactive particle. This shell, as well as high alkali concentration, serves to minimize the amount of calcium hydroxide that can further penetrate the reaction site and precipitate as a non-swelling lime-alkali-silica gel. Verbeck and Gramlich (12) were able to show that the mobility of lime through cement paste was relatively low. On the other hand, they demonstrated that when lime is intimately mixed with reactive materials of fine size, inhibition of expansion may be effective as a result of the formation of a lime-alkali-silicate gel.

## MECHANISM OF EXPANSION

Since the alkali-aggregate reaction was first reported, a number of investigators have developed hypotheses as to the mechanism by which internal pressures are developed.

### Osmotic Pressure Theory

Hansen (10) was the first to propose an osmotic pressure theory. Basically, he suggested that the cement paste surrounding a particle of reactive aggregate acts as a semi-permeable membrane, in that it permits the diffusion of alkali solution and water into the reaction center but restricts the exit of the alkali-silica gel reaction product. Such a theory relies heavily on the assumption that the reaction product is similar to a concentrated solution. Because the reaction product cannot at first escape, fluid pressures are developed which are sufficient to produce cracking and expansion. McConnell and others (15) showed that osmotic pressures of considerable intensity (in excess of 550 psi) may be developed in osmotic cells using sodium silicate solutions in conjunction with cement paste as the semi-permeable membrane. Parsons and Insley (16) showed additional experiments to support the osmotic pressure hypothesis.

### Solid Swelling

Vivian (13) failed to find supporting evidence for the osmotic pressure theory. He was unable to demonstrate the existence of a semi-permeable membrane and therefore the fluid pressures which are necessary to an osmotic pressure mechanism. He attributed expansion to the direct swelling of the solid reactive particle as it underwent reaction and showed that a solid sodium silicate complex is capable of expanding and increasing its volume by about 130 percent by imbibing water and can still remain rigid.

Brown (17) supports these findings and claims that deleterious action is produced by the direct enlargement of the solid reactive particle. He showed that cracks develop within the solid reactive particles and that direct enlargement of these particles will produce expansion cracks within the concrete before any fluid gels appear.

These observations are somewhat supported by the findings of Hurd and Laning (9), who worked with silica gels. They showed that sodium hydroxide will first cause cracks to appear which slowly grow larger and deeper.

#### Solid or Fluid Pressures

Powers and Steinour (5) attempted to reconcile these conflicting views by presenting theoretical and direct evidence for both solid swelling pressures and fluid osmotic pressures depending on the fluidity of the particular reaction product at the time of observation. A solid reaction product may be converted to a liquid product by the continuing reaction with alkalis and imbibition of water. Both are capable of producing pressures. They conclude, however, that the most damaging expansion probably occurs while the reaction product is still solid.

### CHEMICAL INHIBITION OF THE REACTION

Pozzolanic materials have been widely suggested as a promising inhibitor of the deleterious reaction (18, 20, 21, 22). However, Stanton (19) calls attention to the fact that at times some pozzolanic additions may actually aggravate the expansion produced by the alkali-aggregate reaction. Powers and Steinour (14) attempted to explain the beneficial inhibiting effect of pozzolanic materials. They suggested that the pozzolan presents a large area of reactive surface. Thus, the alkali concentration produced by a high-alkali cement is reduced sufficiently to permit a safe reaction (reaction of lime with alkali-silicate products) before the larger reactive silica particles have undergone more than shallow surface reaction.

McCoy and Caldwell (23) found promise in the use of relatively small amounts of chemical inhibitors. Their work showed that lithium salts were effective in preventing expansion of otherwise reactive mortars. More recent work by Verbeck and Gramlich (12) suggests that chemical inhibitors may have some value because of their ability to restrict the movement of alkalis through the cement paste. On the basis of the work done by Pike and Hubbard (7), it was suggested that the inhibiting action of barium and magnesium oxides (released from the aggregates) be further investigated.

### REFERENCES

1. Nekrasov, V.V., and Evko, A.V., Jour. Appl. Chem. (USSR) 20:179-86 (1947); Chem. Abst., 42:23, 1717d (1948).
2. Jones, F.E., Research Paper No. 15, National Building Studies, Great Britain, (1952).
3. Gilliland, J.L., and Bartley, T.R., Jour. Amer. Conc. Inst., 22:2, 153-160 (1950).
4. Rhoades, R., and Mielenz, R.C., Jour. Conc. Inst., 17:6, 581 (1946); Proc. Amer. Conc. Inst., 42:581.
5. Powers, T.C., and Steinour, H.H., Jour. Amer. Conc. Inst., 26:6, 497 (1955); Proc., Amer. Conc. Inst., 51:497.
6. Carman, P.C., Trans. Faraday Soc., 36:964-73 (1940).
7. Pike, R.G., and Hubbard, D., Jour. Res. NBS, 50:2, 127-32 (1957).
8. Vivian, H.E., Austr. Jour. Appl. Sci., 2:1, 108-13 (1951).
9. Hurd, C.B., and Laning, S.H., Jour. Phys. Chem., 58:914 (1954).
10. Hansen, W.C., Proc., Amer. Conc. Inst., 40:213-27 (1944).
11. Pike, R.G., Hubbard, D., and Insley, H., Jour. Amer. Conc. Inst., 27:1, 13 (1955); Proc. Amer. Conc. Inst. 52:13.
12. Verbeck, G., and Gramlich, C., Proc., ASTM, 55:1110 (1955).
13. Vivian, H.E., Part 15, Bull. 256, Commonwealth Scientific and Industrial Research Organization, Australia (1950).

14. Powers, T.C., and Steinour, H.H., Jour. Amer. Conc. Inst., 26:8, 785 (1955); Proc., Amer. Conc. Inst., 51:785.
15. McConnell, D., Mielenz, R.C., Holland, W.Y., and Greene, K.T., Jour. Amer. Conc. Inst., 19:2, 93 (1947); Proc., Amer. Conc. Inst., 44:93.
16. Parsons, W.H., and Insley, H., Jour. Amer. Conc. Inst., 19:8, 625 (1948).
17. Brown, L.S., ASTM, Bull. No. 205, 40 (1955).
18. Lerch, W., ASTM, Bull. No. 99, p. 153 (STP).
19. Stanton, T.E., Porter, O.J., and Nicol, A., Jour. Amer. Conc. Inst., 13:3, 209 (1942); Proc., Amer. Conc. Inst., 38:209.
20. Jackson, F.H., Proc., ASTM, 43:215 (1943).
21. Hanna, W.C., Proc., ASTM, 47:986 (1947).
22. Stanton, T.E., ASTM, Bull. No. 99, p. 78.
23. McCoy, W.J., and Caldwell, A.G., Proc., Amer. Conc. Inst., 47:693.

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