



The potential alkali-aggregate reactivity of Montana concrete aggregates
by Thomas Gould Stewart

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Civil Engineering
Montana State University
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Abstract:

The potential alkali-aggregate reactivity was determined for the fine aggregates from six major concrete aggregate sources in the State of Montana. The aggregates' reactive capacity was determined on the basis of three different laboratory test methods. They were the mortar bar test, the chemical test and the petrographic analysis.

Conclusive evidence showed four of the six aggregates to be reactive and one aggregate to be nonreactive. Results for one aggregate indicated possible reactivity, but the evidence was not conclusive.

Excessive mortar bar expansions occurred for the four reactive aggregates. Three types of low alkali cements, and two types of pozzolans, when tested with these aggregates, demonstrated their ability to prevent this excessive expansion.

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OF MONTANA CONCRETE AGGREGATES

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THOMAS G. STEWART

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fulfillment of the requirements for the degree

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ABSTRACT

The potential alkali-aggregate reactivity was determined for the fine aggregates from six major concrete aggregate sources in the State of Montana. The aggregates' reactive capacity was determined on the basis of three different laboratory test methods. They were the mortar bar test, the chemical test and the petrographic analysis.

Conclusive evidence showed four of the six aggregates to be reactive and one aggregate to be nonreactive. Results for one aggregate indicated possible reactivity, but the evidence was not conclusive.

Excessive mortar bar expansions occurred for the four reactive aggregates. Three types of low alkali cements, and two types of pozzolans, when tested with these aggregates, demonstrated their ability to prevent this excessive expansion.

CHAPTER I

INTRODUCTION

For the past twenty years alkali-aggregate reaction has been an important subject in the study of concrete durability. The reaction occurs between the alkalies, released by the hydrating cement, and susceptible siliceous rocks and minerals in the aggregate. The product of this reaction is an alkali-silica gel which has the property of swelling through osmosis. This action can cause expansive deterioration of the concrete. When expansive deterioration occurs in a relatively short time, the identification of alkali-aggregate reactivity is usually unmistakable due to the characteristic pattern cracking and the exudation of silica gels appearing on the surface of the concrete. However, in most cases, deterioration occurs over a considerable period of time. Positive identification of the original cause of deterioration is then obscured by the multitude of factors involved.

Successful corrective measures have been used to counteract the alkali-aggregate reaction. Three of these measures are: the use of non-reactive aggregate, the use of low alkali cement, and the use of pozzolanic additives.

A few concrete structures in the State of Montana are experiencing minor deterioration, but it is difficult to relate the cause of deterioration directly to alkali-aggregate reactivity. In 1950, a concrete durability study was insti-

tuted at Montana State College in co-operation with the Montana State Highway Commission. Tests were included in the durability study to determine the potential reactivity of various aggregate sources. The results of these tests are presented in a Master's Thesis written in 1952 at Montana State College by R. A. Wallace.

An accelerated mortar bar test and a chemical test were used to determine the potential reactivity of the aggregates. The chemical test showed that seven out of nine aggregate sources tested were potentially reactive. However, the corresponding mortar bar tests failed to give significant expansions to support the chemical tests. On this basis, it was not possible to make definite conclusions concerning the potential reactivity of the aggregate sources. The author felt that further investigation of the potential alkali reactivity of the aggregate sources would be of considerable importance.

The primary purpose of this thesis was to evaluate, based on laboratory tests, the potential alkali-aggregate reactivity of six major concrete aggregate sources. These included five of the nine sources used in the previous durability study by Wallace.

The secondary purpose of this thesis was to evaluate, based on laboratory tests, the capabilities of three common

cement types and two pozzolan materials in preventing expansive reaction with any aggregate sources found to be potentially reactive.

One of the most common practices for controlling alkali-aggregate reactions is to use only low alkali cements with all concrete aggregates. However, this practice cannot be justified in all situations without the knowledge of an aggregate's reactive capacity, since, in some cases, this practice may be unwarranted; while in others, inadequate. The following considerations indicate that it is desirable, and, in certain cases, necessary to have knowledge of an aggregate's potential reactivity:

1. Researchers express concern over the question of what percentage of alkali in the cement would be safe for all types of aggregate, or, what is actually the safe dividing line between low and high alkali cements. The safe dividing line could be established for a given aggregate source with a knowledge of the aggregate's potential reactivity.
2. The amount of alkalies present in Portland Cement depend primarily on the natural characteristics of the quarry material used in the production of the cement. Material high in alkali content can be controlled in the production process, but it is not economically feasible to eliminate all the alkalies. Since a certain amount of alkalies are always present, it would be desirable to know the potential reactivity of a given cement and aggregate.
3. Certain aggregate material may be the source of additional alkalies which could raise the total alkali content in a concrete mix to a potentially dangerous amount. In such cases knowledge of the

potential reactivity of the aggregate would be necessary to design a safe mix.

4. If the aggregate is known to be reactive, low cost pretested additives can be used as a safeguard without knowledge of the alkali content of the cement. This is an advantage to smaller organizations who do not have facilities to check alkali contents in cements.
5. Concrete made with low alkali cements and reactive aggregate usually experiences a limited reaction. Little is known as to whether this limited reaction significantly contributes to poor concrete durability. An evaluation of the aggregate's potential reactivity with low alkali cements would aid in determining the effects of a limited reaction.

Awareness of the alkali-aggregate reaction was a result of rapid deterioration of certain costly concrete structures. Knowing the potential reactivity of concrete aggregates enables one to make the proper selection of materials to assure against similar occurrences in the future. It is hoped that the results of this investigation can be used to further improve the durability of concrete in the State of Montana.

Chapter II presents a review of literature on the subject of alkali-aggregate reactivity with emphasis on the progress made on the subject in the past ten years.

The first part of Chapter III describes the equipment and materials used for the laboratory studies. The second part of Chapter III describes the planning of the laboratory tests and the procedures used.

Chapter IV gives the results and interpretation of the laboratory investigations. The first half of the chapter is an evaluation of all tests conducted for the purpose of determining the potential reactivity of the aggregates. The second half of the chapter is an evaluation of the low alkali cements and pozzolans tested for the purpose of counteracting the alkali-aggregate reactivity.

Conclusions and recommendations for further investigation appear in Chapter V.

CHAPTER II

THE REVIEW OF LITERATURE

In 1940, the cause of certain badly distressed concrete structures was determined to be an expansive reaction between water soluble sodium and potassium alkalies of the cement and various forms of siliceous materials in the aggregate. This initiated some extensive research that was mainly directed to seeking out the types of potentially reactive aggregate, developing tests to predict the suitability of the cement and aggregate, and testing various additives to prevent incompatible cement-aggregate combinations from reacting. Theoretical considerations of the reaction were secondary, and the few hypotheses set forth to explain the phenomena lacked supporting evidence. Due to both the complexity involved in the exact interpretation of the alkali-aggregate reaction and the lack of standardized tests, laboratories engaged in similar studies sometimes presented anomalous results. In general, by 1950, enough knowledge of the alkali-aggregate reaction had been gained to prevent a recurrence of any dramatic and costly damage.

Much remained to be done to more thoroughly understand, evaluate and control the reaction. From roughly 1950, to the present, a considerable amount of the research was directed to the theoretical considerations in an attempt to put the explanation of the phenomena on a sound basis. The

hypotheses presented were supported with newly designed laboratory techniques, and the earlier more reliable laboratory tests for potential reactivity were refined to give suitable test correlations and to give understandable reasons for any non-correlations. In recent years valuable long-time test results from various laboratories are appearing in the publications.

The discussion of the literature between 1940 and 1950 covers particularly well established facts. Results that have been of major controversy are also presented and reviewed in light of the more recent progress, which comprises the major part of the review. The discussion will include:

1. The general nature of the reaction and important factors influencing it.
2. The development and use of the most reliable tests to determine the reactive potential of aggregates.
3. The known types of reactive minerals and rocks and their relative degree of reactivity.
4. The most widely used methods to prevent the occurrence of harmful alkali-aggregate reaction in concrete.

THE NATURE OF THE REACTION

It has been found that the reaction is basically a progressive chemical attack by an alkali hydroxide on particular forms of silica present in the aggregate.

The chemical reaction and the product formed have been

clearly and fundamentally explained by T. C. Powers and by H. H. Steinour (23).¹ In order to carry out their explanations they imagined, for simplification, that only a hydrous silica particle surrounded by sodium hydroxide solution was present. The interior portion of the silica particle would consist of silicon atoms surrounded, in a tetrahedral configuration, by four oxygen atoms. At the surface, however, the oxygen atom could only be bonded by one silicon atom instead of two. The resulting surface would consist of oxygen ions having one unsatisfied negative charge and silicon ions having one unsatisfied positive charge. This condition would bring about a surface hydration in the presence of water, i.e., one hydrogen ion joining the oxygen ion and the left-over hydroxyl ion joining the silicon ion. The hydrogen ion that joined the oxygen would be loosely bonded, and in an aqueous medium the surface would ionize to form a silica particle of weak acidity. Mr. Powers discussed the nature of reaction of such a particle in the presence of sodium hydroxide, a strong alkali. The initial reaction would be an acid-base neutralization, since the surface of the silica particle is acidic. If the sodium hydroxide concentration was strong, it would not only remove and neutralize the

¹ Figures in parenthesis indicate references on page 178.
(LITERATURE CITED)

surface hydrogen ions, but also break silicon-oxygen-silicon linkages, forming a new surface susceptible to attack and identical to the initial surface of attack. Thus the particle would be reduced to a gel substance with the silica in the form of colloidal particles which Powers called a "silica sol".²

The resulting softened gel-like product contains sodium, silicon, and oxygen, and when any alkali is involved it is commonly called an alkali-silica complex. This complex is capable of imbibing water and swelling. It has been shown that this swelling is capable of producing pressures within concrete sufficient to rupture the concrete, and is believed to be the fundamental cause of the expansion in concrete experiencing alkali-aggregate reaction.

MECHANISM OF EXPANSION

The mechanism by which this expansion occurs was first postulated by W. C. Hanson (10) to be an osmotic phenomena.

²A general term and definition for this particular type of sol defined by Hiller and Herber (14) is a "Lyophilic sol" -- "A solution of high polymers dispersed molecularly in suitable solvent. Such a sol is made up of particles that have an attraction to the liquid medium and tend to disperse spontaneously by a process called 'Peptization'." Hiller and Herber define a gel as a semisolid elastic structure which contains large amounts of solvent loosely held together by an open network of solute molecules where solvent and small solute particles can readily migrate through the gel structure, demonstrating properties not greatly different from liquids.

He considered the alkali-silica complex around a reactive particle a solution, water a solvent, and the mortar about the particle a semi-impermeable membrane, and that the actual expansion of the concrete was due to hydraulic pressures produced through an osmotic transfer of water to the solution side of the membrane. The net effect of osmosis as described by Hiller and Herber (14) is to cause a transfer of solvent molecules through the pores of a semi-permeable membrane to the solution side; the actual motion being due to an unequal vapor pressure between the areas separated by the membrane. The hydrostatic pressure required to balance the process is termed the osmotic pressure of the system. The difference in vapor pressure is explained in terms of a kinetic mechanism in which the solvent atoms that are in the solute (the solution side) have a lower energy level than the pure solvent side. Thus, there would be fewer collisions of the solvent atoms on the solution side of the membrane than there would be on the pure solvent side, resulting in a net movement of solvent atoms to the solution side. The relative vapor pressures then would be a measure of the available energy in the solvent side that could be imparted to the solution side. Powers and Steinour used this explanation to further support Hanson's osmotic pressure theory. They considered the alkali-silica complex a solution containing water that

is lower in energy than the free water in the mortar. The net effect would be a migration of free water to the solution area with consequent swelling of the alkali-silica complex. If the alkali-silica complex (usually in the form of a gel) were sufficiently confined, pressures high enough to rupture the concrete could be produced before reaching the osmotic pressure required to equalize the process.

Hanson attributed the entire expansion to this hydrostatic pressure of a confined gel deposit. However, Brown (7) maintained that the major portion of harmful concrete expansion was due to direct swelling of the aggregate particles. Verification of this was attempted with the presentation of some photographs of thin sections sawed from highly reacted concrete and mortar bars. These showed altered reacted particles with characteristic reaction rims along with sharply defined cracks through an unreacted internal portion. These cracks stopped abruptly at the internal edge of the reaction rims. Radial cracks extended out through the mortar from the reacted particles, with some reaching the surface of the concrete specimen.

The important observation by Brown was that these particles were obviously causing the greatest expansion in the concrete and were the source of most surface cracks. Sharply defined cracks in the internal portion of these reacted

particles were lacking signs of gel. Brown suggested that the reaction rim, while still in a highly viscous stage, produced swelling sufficient to cause harmful expansions. The attack on a particle was presumed to proceed inward, thus the viscosity of the reaction rim would increase inwardly, and the tendency would be for the less viscous or more liquid gel to move outward through the radial cracks to the surface, or to available air pockets in the matrix.

The hydrostatic pressure of a confined deposit of a liquid gel might then be considered a secondary cause of disruptive expansion. However, as Powers pointed out, the line of demarcation between the softened solid reaction rim and a liquid gel is not clearly distinguishable, nor is the interpretation of hydrostatic pressure of such a substance.

For the purpose of describing the basic alkali-aggregate reaction and the formation of the alkali-silica gel complex capable of swelling, Powers and Steinoor imagined that only the sodium or potassium alkalies were available. The acid-base neutralization of sodium or potassium ions previously referred to could also take place with the calcium ions which are abundant in cement mortar. This would produce a lime-silica complex, or more likely a lime-alkali-silica complex, since ions of both are present. It has been shown, depending upon the amount of calcium hydroxide in the complex, that the

reactive products of the lime-alkali-silica complex are relatively insoluble, and that the gel formed is incapable of the unlimited swelling associated with alkali-silica gel.

It has been concluded by most investigators that an alkali-silica complex must be formed to cause alkali-aggregate expansion in concrete.

FACTORS INFLUENCING THE EXPANSION OF CONCRETE DUE TO THE ALKALI-AGGREGATE REACTION

The Lime-Alkali-Silica Complex

Probably the most important factor influencing the degree of expansive reaction is the relative amounts of alkali-silica complex and lime-alkali-silica complex that can be formed in a potentially reactive cement and aggregate mix. More specifically, the type of reaction product is in relation to the relative amounts of sodium and calcium that can diffuse into the reaction site. Although there is always a great abundance of the calcium ion available, the alkali-silica complex still manages to form. This suggests that there must be a hindrance to the diffusion of the calcium ion to the reaction site.

From the evidence of experimental data, Powers and Steinour (23) conclude the following reason for this hindrance of calcium ion diffusion:

"It thus seems to be established that the initial attack of the alkali and lime builds up a zone of lime-alkali-silica complex which, when it reaches requisite thickness, hinders the diffusion of cal-

cium ions across the boundary region of the reactive particle, but at the same time allows alkali and water to pass. This enables deposits of pure alkali-silica complex to form and remain in concrete for an indefinite period."

Shortly after the publication of Powers and Steinour (23), there appeared an interesting and valuable osmotic pressure study by G. S. Verbeck and C. Gramlich (26). They concluded that the degree of calcium ion diffusion to the reaction site depended upon the difference in the availability and mobility of the calcium ions and the ions of sodium and potassium. Due to this concept of availability and mobility, they felt that the reaction of calcium and alkali ions with the silica proceed on a competitive basis. The effect of calcium hydroxide was studied by adding increasing equal amounts of solid calcium hydroxide to two osmotic chambers containing a fixed amount of sodium hydroxide solution.³ The reaction chamber, in addition, contained opal as the reactive aggregate. The

³To arrive at their conclusions they devised a simplified osmotic apparatus consisting of the following: Two chambers separated by a membrane of cement paste. Reactive aggregate, solid calcium hydroxide and alkali solution are placed in one chamber to simulate the zone at the surface of aggregate in concrete. In the other chamber, separated by the cement paste membrane, additional solid calcium hydroxide and alkali solution are added. Capillary tubes are attached to each chamber enabling measurements of the flow rate through the membrane brought about by the reaction product imbibing water and swelling. The osmotic pressure is the hydrostatic pressure required to stop the flow of liquid through the membrane.

results showed a marked decrease in flow rate (expansive reaction) with increased calcium hydroxide addition. The important observation was that it took an exceedingly large amount of $\text{Ca}(\text{OH})_2$ to decrease the flow rate, and that this amount was far more than necessary to make the complete reaction a non-expansive calcium silicate reaction. The tests were further extended by comparing these results with the flow rate resulting from mixing the calcium hydroxide with the aggregate. The mixed sample gave a significant reduction in flow rate. Therefore, it was assumed that, in order for the reaction to be of the non-expansive calcium silicate type, the calcium hydroxide must be in very close proximity to the reaction site. These results were sufficient to conclude that the calcium hydroxide ions have a considerably lower mobility in aqueous solutions than the sodium hydroxide ions. Verbeck and Gramlich attributed the mobility rates to a phenomena called "hydration of ions" in aqueous solution, in which the ion surrounds itself with a sphere of water molecules. This effectively increases the total size of the ion's influence and decreases its mobility. Table I, taken from Verbeck and Gramlich's paper shows a definite correlation between the observed flow rate (expansive reaction) and the ion hydroxide of the pertinent ions.

TABLE I

OSMOTIC FLOW RATES AND HYDRATION VALUES FOR VARIOUS IONS

Hydroxide	Average Rate of Flow Cm. per day per 1% sodium hydroxide equivalent	Average number of H ₂ O molecules per ion
Potassium	0.70	5.4
Sodium	0.53	8.4
Lithium	0.24	14.0
Calcium	-----	24.0

Pessimum Amount

It had been demonstrated by Vivian (23), and verified by others that by keeping the amount of alkali constant and increasing the percentage of reactive component of the aggregate a "harmful optimum", or "pessimum" percentage exists which will give the maximum expansion in mortar bar specimens. Depending on the alkali concentration and the type and amount of reactive component, pessimum proportions of the reactive component have been found ranging from as little as 0.5 per cent to 100 per cent in aggregates tested.

It is believed that percentages of reactive material ranging from zero to that giving the pessimum amount increases the expansion due to the increasing amount of available

surface area of reactive material. The decrease in expansion from the maximum by a further increase in the percentage of reactive material is explained by Verbeck and Gramlich, based on their osmotic cell studies:

"As the amounts of reactive aggregate increases, the alkali per unit area will be reduced while the calcium hydroxide available per area surface will remain essentially constant, since it is only that particular calcium hydroxide immediately adjacent to the surface that is available for reaction. The ratio of available alkali to available calcium hydroxide is, therefore, reduced and lesser proportions of the deleterious alkali silicate are produced as the gross quantity of reactive aggregate is increased."

The proportions necessary to obtain the pessimum amount are relatively critical and are dependent on many factors. It is apparent that consideration must be given to the pessimum phenomena in the analysis of field and laboratory specimens or for evaluations of aggregates to be used in future projects. Some inaccurate conclusions were made in test results before this important factor was discovered.

Degree of Reactivity of Potassium and Sodium Alkalies

There has been some discrepancy in literature as to the degree of reactivity of potassium and sodium alkalies contributing to the total expansion of concrete. Mr. Lerch (15) found that sodium hydroxide gave greater expansion than potassium hydroxide when tested using mortar bar prisms with

graded Pyrex glass as aggregate.⁴ Verbeck and Gramlich (26) acknowledge that from the consideration of the standard electromotive series of the alkalies, one would estimate, and as Lerch had found, sodium to be the greatest contributor. However, they evidenced just the reverse in their osmotic cell studies. Their conclusion was that the potassium ion had greater mobility due to the lesser ion hydration of the potassium ion. This can be seen in Table I on page 16.

In view of the more recent results found by Verbeck and Gramlich, it is possible that the earlier findings of Lerch can be logically explained. Since the aggregate consisted entirely of reactive aggregate, mobility of the alkali ions would most likely not be a factor since the alkali hydroxides would already be in close contact with reactive particles. Therefore, since the sodium alkali is higher in reactivity on the electromotive series, a more reactive attack by the sodium than by the potassium would account for Lerch's results. The percentage of reactive particles in actual concrete aggregate is small and movement of the alkali ions to the reaction sites would depend considerably on the mobility factor. Therefore, it appears that potassium over sodium would be the likely order of reactivity in concrete.

⁴Pyrex Glass is a reactive silica glass capable of producing abnormal expansion when used as an aggregate.

There is an interesting point bearing on this recent finding. At present, the widely accepted method of expressing the total sodium and potassium oxides of the cement is based on sodium being the most reactive. The reactive capacity of the combined effects of sodium and potassium oxides is expressed as a sodium equivalent. The method is described in the Bureau of Reclamation's 1951 Concrete Manual (24):

"Sodium and potassium are both undesirable components of cement, but a given weight of Na_2O is more active than the same weight of K_2O , each per cent of K_2O being chemically equivalent to 0.658 per cent of Na_2O . This relationship enables the total alkalis in cement to be expressed as a single equivalent percentage by weight, computed as the sum of the percentage of Na_2O plus 0.658 times the percentage of K_2O ."

It is possible that, in the future, this method will be modified to account for the mobility of the ions.

Effects of Water-Cement Ratio

Until recently very little information has appeared in the literature directly related to the effect of the water-cement ratio on the expansion associated with alkali-aggregate reactivity. It appears that the water-cement ratio affects both the alkali concentration and the permeability of the cement paste, which, in turn, affects the expansive reaction.

Lerch (15) hypothesized that the abnormal expansion of concrete depended upon the alkali hydroxide concentration in the free water, and that, with a fixed amount of alkali, the

