

COMMENTS ON THE PAPER

"CHEMICAL REACTIONS INVOLVING AGGREGATES"

(Bredsdorff, et al)

by

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DISCUSSION OF PAPER ONE - SESSION SIX

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The discussion presented below concerns the section on "Unidentified Cement-Aggregate Reactions" in which mention is made of concrete deterioration related to argillaceous dolomitic limestone aggregates. A considerable amount of research has been conducted on carbonate aggregate-cement reactions as part of the general study on the suitability of carbonate rocks as concrete aggregate which inadvertently did not reach the authors in time to be incorporated in their paper. These reactions which occur in response to the alkaline environment of concrete are not typical alkali-aggregate reactions associated with siliceous aggregates such as opaline cherts, volcanic glasses and etc. The reactions are associated with certain carbonate aggregates whose service records indicate deleterious performance in concrete has occurred. It is my purpose to review briefly carbonate aggregate research conducted at Iowa State University and present some new data on the problem of carbonate aggregate-cement paste reactions.

Although a considerable amount of material has been published on concrete aggregates, few deal specifically with carbonate aggregates. One of the first papers on carbonate aggregate was written by Laughlin<sup>(1)</sup> in 1928. Other work by H. S. Sweet<sup>(2)</sup>, B. Mather, et al<sup>(3)</sup>, K. Mather<sup>(4)</sup> dealt directly with carbonate rocks emphasizing the petrographic and physical aspects. Within the past five years however the recognition that certain carbonate aggregates contribute to distress in concrete because of chemical reaction has led to

participation in research by several other groups in the United States and Canada. Significant contributions have been made by Swenson and Gillot<sup>(5)</sup> on the Kingston aggregate in Canada, by Hadley and others under the direction of Verbeck at the Portland Cement Association Laboratories and by Chaiken and Halstead<sup>(6)</sup> of the Bureau of Public Roads. Their work emphasizes the expansion of carbonate rocks in alkaline environments and especially the reaction of carbonate minerals or "dedolomitization" with alkalies.

Because of direct correlation of poor service record of certain Iowa highways to coarse carbonate aggregates from certain quarries, studies sponsored by the Iowa State Highway Commission were first begun in 1948 by Dorheim<sup>(7)</sup> who by means of expansion tests on concrete bars, concluded that clay in limestone might be indicative of poor performance. Work was continued by Roy, et al<sup>(8)</sup> who made a petrographic study of the Mississippian carbonate rocks which included those from LeGrand with a poor service record. Although there was no correlation of petrographic characteristics with service record, they observed that weathered aggregates with increased absorption were associated with distressed concrete.

In 1955 the research was renewed and investigation of Devonian rocks from the Glory quarry which produced rock with a notoriously poor service record led to publication by Lemish, Rush, and Hiltrop<sup>(9)</sup> on the physical properties of the aggregates. They concluded that impure carbonate rocks characterized by high residue and clay content were poor aggregate and they postulated that pore-size distribution of the rock was important to serviceability. Examination of deteriorated concrete indicated that the softer matrix was carbonated and impure coarse carbonate aggregates were characterized by reaction shells. Bisque and Lemish<sup>(10)</sup> also described the chemical properties of carbonate rocks as related to durability of concrete and found that reaction shells

were silicified and selectively formed on aggregate containing clay, a high percentage of insoluble residue, high magnesium content, and higher amounts of silica. They reported a method of growing reaction shells on these impure carbonate rocks in silica-rich solutions at pH 12 and demonstrated carbonate rocks reacted chemically in concrete environments.

Further study by Hiltrop and Lemish<sup>(11)</sup> conducted on the relationship of pore-size distribution and other rock properties to serviceability, led to the conclusion that pore-size distribution alone is not indicative of performance as an aggregate but that the presence of clay and the Ca/Mg ratio were definitely related to serviceability.

Continued study by Bisque and Lemish<sup>(12)</sup> demonstrated that reaction shells could be experimentally grown on impure aggregates in concrete bars and that shell growth in the instance of Glory aggregate was due to introduction of silica from cement paste. Shells were also grown rapidly in cement paste bars by Lemish<sup>(13)</sup> in an autoclave. Further studies<sup>(14)</sup> indicated that sodium and potassium were not introduced into the shell and that bars in which shells were grown had no increase in compressive strength accompanied by no excessive expansion. It was postulated by Bisque<sup>(15)</sup> and demonstrated by Hiltrop<sup>(16)</sup> by means of silicon tetrachloride and vaporous organic silicone compounds that silica introduced into the rock could be stabilized or fixed by clay particles.

In recent unpublished research at Iowa State University under the direction of Lemish, Harwood<sup>(17)</sup> continued the study by measuring compositional variations in aggregate and cement resulting from carbonate aggregate-cement paste reactions. A series of different aggregates cut in the shape of a cube were placed in cement paste bars of Type I cement (.52% alkali reported as Na<sub>2</sub>O) and were soaked continuously in distilled water at 55° C for three months. Two cubes of reactive Glory aggregate were similarly reacted with

cements consisting of alite ( $3\text{CaO}\cdot\text{SiO}_2$ ) and belite ( $2\text{CaO}\cdot\text{SiO}_2$ ) respectively at a pH 12 environment. Chemical analyses and X-ray studies were made on samples taken at specified intervals across the aggregate into the cement paste.

Fig. 1 gives the summary of silica behavior for different types of aggregates.

Silica shows variable behavior. In the case of the Glory aggregates which served as a basis for Bisque's work, silica increases in the reaction shell, and shows a drop in the cement paste. This is true for the Newton aggregates. Both aggregates can be characterized as dolomitic lower to moderate insoluble residue types. In the Kenwood aggregate, a rock which behaves like the Kingston aggregate and is dolomitic with a high silica-rich residue, the reaction shell decreased in silica content and silica increased in adjacent cement paste. Regardless of how silica varied, a resistant silicified shell of amorphous silica results. In all cases magnesium migrates from the shell zone and some calcium migrates into the shell from the cement.

The cubes of Glory aggregate placed in alite and belite showed a behavior different from that when placed in portland cement. Silica was removed from the same type of aggregate which characteristically gained silica when placed in portland cement bars indicating that alite and belite are not the source of silica in the shells.

X-ray data of the shell zone indicate quartz and dolomite decrease; calcite increases. In some instances some  $\text{Ca}(\text{OH})_2$  was found in the shell. In the immediately adjacent cement, the hydrated cement compounds showed a more disordered pattern.

Harwood's data suggest that silica migration is essentially an equilibrium reaction controlled by (1) the relative concentration of available silica in adjacent aggregate and cement and (2) by the local pH environment.

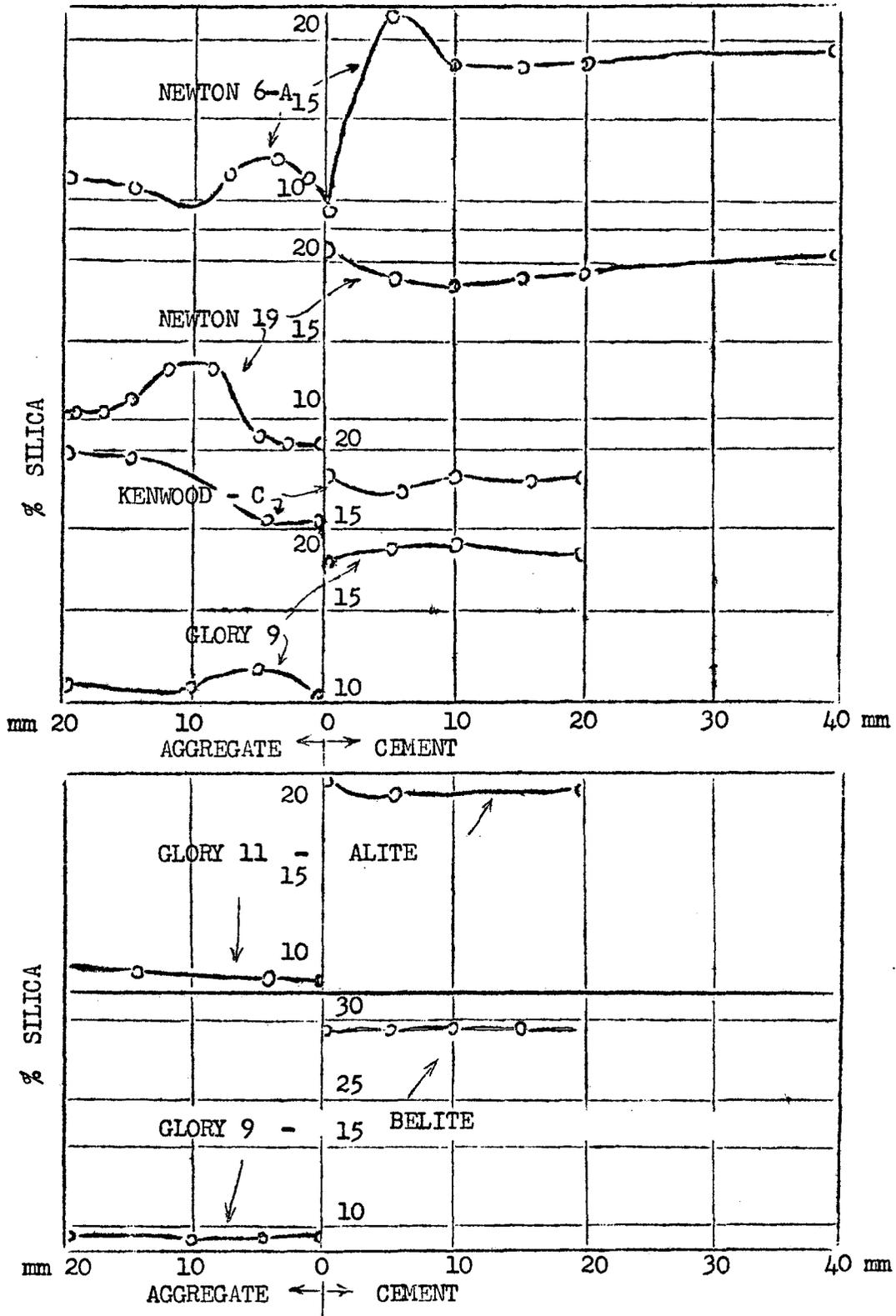


Fig. 1 - SILICA VARIATIONS

The dolomite-hydroxyl ion reaction (dedolomitization) explains the dolomite decrease and calcite increase in the shell. Some calcite could form through the introduced  $\text{Ca}(\text{OH})_2$  or Ca ions with  $\text{CO}_2$  released during the reaction. Aggregates with low insoluble residue do not extract silica because they lack sites for silica precipitation or fixation and generally would have a good service record.

This latest research indicates silica appears to move either way, and all components of a carbonate aggregate are affected by alkali reaction. It emphasizes that several changes occur in the shell zone simultaneously. Shell formation does not mean a definite increase or decrease in silica content; it signifies the formation of amorphous silica.

Interesting as these data are, it must be pointed out that during all of Harwood's experiments it was assumed that the composition of the rocks was uniform and representative. One of the major problems in these studies is the experimental and quantitative controls needed to be positive of the direction of ion migration and compositional changes before and after an experiment. Since most of the quantitative methods of analysis are destructive, the initial composition must be assumed to be uniform and representative of similar materials.

In order to get around some of these experimental difficulties and to study silica behavior more accurately Hiltrop<sup>(18)</sup>, as part of his Ph.D. thesis research under Lemish, adapted a refluxing technique to measure silica more representatively. In an attempt to learn the form that the available silica or "silicate" is in and the conditions under which it migrates in and out of rocks, he applied the concept of "reactive" and nonreactive" silica on the basis of the ammonium molybdate method<sup>(19)</sup> of silica determination and subsequent hydrofluoric acid treatment. After measuring the amount of silica in

solution contributed by an aggregate by the ammonium molybdate method, it was found that HF treatment always increases the soluble silica present, indicating that more complex unavailable species of silicate are present. The immediately available species (probably monomeric silicate) was called molybdate "reactive" silica and the more complex HF treated silicate, molybdate "nonreactive" silica.

Refluxing different deleterious aggregates in glass vessels at pH 12 produced varying amounts of reactive versus nonreactive silica. Hiltrop found that glass vessels produce 100% "reactive" silica in large amount. Cement pastes when refluxed in glass at the same conditions as the rocks produces very small amounts of total silicate in solution, a large proportion of which is nonreactive and is accompanied by a coating of a calcium silicate compound on the walls of the reaction vessel.

This promising line of attack is being carried out in silica-free refluxing vessels and it may show promise as a means of differentiating the potential reactivity of an aggregate in a manner more positive than present testing methods.

#### SUMMARY

The research at Iowa State University raises more problems than answers. Research to date shows that cement-aggregate reaction is selective and that dolomitic argillaceous carbonate rocks characterized by relatively high residues react with cement. All the components of the rock react to form a silicified "dedolomitized(?)" shell.\* Silica can move in or out of an aggre-

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\* Magnesium may also come from a high magnesium calcite

gate and an attempt to study the form of the silica or "silicate" had led to the concept of molybdate "reactive" and molybdate "nonreactive" silicate.

Several problem areas remain where research needs to be done:

1. A need exists for more data on behavior of Na and K in shell zones.
2. More data are needed on behavior of silica and conditions under which it migrates.
3. Data are required on sources of readily available silica in rock and cement.
4. More data on the true nature of carbonate rocks, especially mineralogical composition, texture, structure, and geological relationships.
5. The relation of carbonate aggregate-cement reactions to performance of concrete.
6. Most important of all, knowledge of how alkali-induced reactions contribute to distress in concrete.

With regard to this last point, present information indicates that (excluding physical damage) distress can be produced by expansion, changes in the concrete or cement matrix, or a combination of both. If alkali reactions occur in the aggregate producing amorphous or some form of soluble silica which in turn may swell or expand because of osmotic processes, one can visualize that it is not the excessive amount of reactive silicate minerals which need be present, but the critical relationship between the size of the pore to the reactive silicate material present. A small amount of silica reacting in a small enough pore could cause enough confinement to produce expansion. This may be why some of our impure carbonate aggregates do not respond to the traditional alkali reactivity tests which are being used.

One could also visualize that if silica is extracted from the cement, that a gradual weakening of the concrete would result. Evidence that concrete in which carbonate aggregate-cement reactions have occurred does not gain strength during curing supports this possibility. Changes brought about in

the cement during the reaction might even condition the concrete to later secondary changes which could also cause additional expansion or deterioration.

Considerable progress is being made in carbonate aggregate research but the greatest gain to date this work has accomplished is the awareness that many types of reaction can and will occur when an aggregate is placed in concrete. The concept of cement-aggregate compatibility is more meaningful.

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