

# Silicification of Carbonate Aggregates in Concrete

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It is demonstrated that the types of carbonate aggregate from the Cedar Valley formation in Iowa which have been classed as acceptable or unacceptable on the basis of service records, can also be differentiated on the basis of their reactivity with silica and/or fluoride in aqueous solution. This reactivity is generally directly related to the purity of the rocks as regards the amount of acid-insoluble material present. It is also shown that reaction shells such as those which appear in unacceptable aggregate in distressed concrete can be experimentally "grown" by placing these aggregates in concrete bars and subjecting them to controlled laboratory conditions. That reaction shell growth is due primarily to the introduction of silica derived from the cement paste is demonstrated by placing aggregate chips in equilibrium with cement paste at 125 F for 50 days and comparing the amount of silica present in the aggregate before and after this treatment. A definite weight increase in the aggregate chips is also noted. The possibility that the silica may have been derived from the fine quartz aggregate was studied experimentally with negative results.

● THIS report is the result of a continuation of the investigation described in HRB Bull. 196 (1958). This portion of the study is aimed at determining the nature of the chemical activity which results in the growth of reaction shells in certain deleterious carbonate aggregates. A description of these shells, supplemented by photographs and photomicrographs, is contained in a report by Lemish et al (7).

In their first report the authors postulated, on the basis of experimental evidence, that the reaction shells are due to the introduction of silica into the aggregate particle. It was suggested that the silica was derived from the cement paste. The extent of the investigation at the time did not warrant presentation of any definite conclusions. It is felt that the additional data and observations included in this report will substantiate the original proposal that silica is introduced into these carbonate aggregates from the cement paste. This reaction must be differentiated from the commonly referred to "alkali-aggregate reaction" which involves the attack of reactive silica in aggregates by alkali derived from the cement paste (4, 6, 8, 9).

## EXPERIMENTAL RIM GROWTH IN AQUEOUS SOLUTION

It can be shown that the type of aggregate which develops reaction shells in distressed concrete does actually "consume" silica from a dilute aqueous solution of sodium silicate at pH 10-12. The pH of a solution resulting from the equilibria established between neat cement paste and distilled water is 11.5 or higher. The depletion of silica concentration due to the presence of these aggregates was reported in HRB Bull. 196 (1). The reported silica determinations were made gravimetrically. Because very small changes in silica concentration are involved it is more desirable to utilize a spectrophotometric determination (2). Such spectrophotometric determinations have been made and the results substantiate the data arrived at via the gravimetric procedure. The rate of decrease in silica concentration due to the presence of (a) a type carbonate aggregate which does not develop reaction shells in concrete; and (b) a type which does (1) is plotted in Figure 1. These curves were arrived at in the following manner.

Carbonate fragments passing a 4-mesh sieve and retained on a 6-mesh sieve were washed and saturated with distilled water. One hundred grams of a given type aggregate

was placed in each of a series of polyethylene bottles and equilibrated with equal volumes of a  $5 \times 10^{-4}$  M sodium silicate solution at pH 10. Samples of the solutions were taken at the indicated time intervals and analyzed for silica. Although no precipitate formed in the solution, the silica concentration was gradually depleted as shown. The extent of depletion was found to vary with the type of carbonate rock used. Curve A (Fig. 1) shows the depletion caused by aggregate from the Coralville member of the Cedar Valley formation in the Glory Quarry (1); and Curve B, the depletion caused by aggregate from the lower Rapid member of the same formation. The average chemical composition of the lithologic units in these members is given in Table 1.

TABLE 1

Member	% CaCO <sub>3</sub>	% Mg CO <sub>3</sub>	% Insol. Residue
Coralville	90.5	5.5	2.8
Lower Rapid	63.5	20.5	13.7

Hence there is an indication that the impure carbonate rocks are more susceptible to "attack" by silica in solution. The fact that silica has actually "entered" the carbonate fragments can be demonstrated by breaking the fragments to expose a fresh surface and etching this surface with hydrochloric acid. The "shell" of the particle is considerably less soluble than the unaffected interior and stands in relief after etching. Photographs of these rims are included in the previous report.

### FLUORIDE REACTIVITY

The reactivity of these rocks was further investigated by determining their susceptibility to replacement by fluoride from dilute hydrofluoric acid solution and comparing this with their susceptibility to reaction with silica. Since the fluoride ion replaces the carbonate in the lattice of a carbonate rock to form fluorite (CaF<sub>2</sub>) and/or sellaite (MgF<sub>2</sub>), it was reasoned that a determination of susceptibility to replacement by fluoride might prove to be an index of "purity" of a carbonate rock. The results of determinations of susceptibility to silica and fluoride activity for six rocks of varying character are shown in Table 2.

An inverse relationship between fluoride and silica "consumption" is apparent and the changes in activity are more closely related to the insoluble residue content than to the magnesium content. The differences might be attributed to some variable within the insoluble residue, such as clay. The determined decrease in fluoride activity which accompanies an increase in insoluble residue is greater than could be attributed

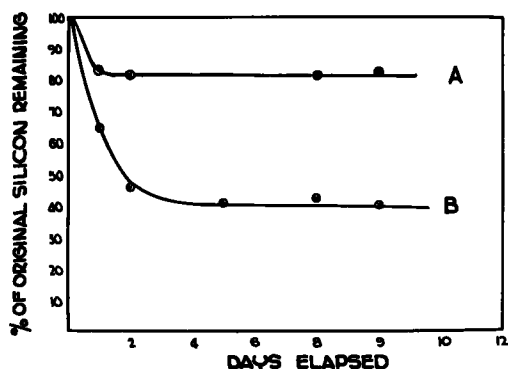


Figure 1. Depletion of silica concentration caused by two contrasting types of carbonate aggregate.

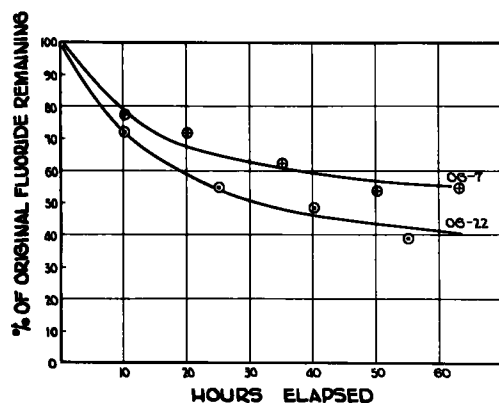


Figure 2. Depletion of fluoride concentration caused by two different carbonate rocks.

to mere "dilution" of the carbonate lattice by the presence of non-carbonate particles such as chert or seams of clay. In other other words, referring to Table 2, if 14 percent of sample 7 were removed before determination of the fluoride reactivity, the percent of total fluoride consumed would not decrease to 25 percent as is the case for sample 3 which has an insoluble residue content of 14 percent.

Reasons for the differences in reactivity toward silica and fluoride are not completely clear but the following points are of interest: (a) there is a general inverse relationship between the two types of reactivity; (b) the types of carbonate rocks which are differentiated by the presence or absence of reaction shells in distressed concrete (1) are also differentiated on the basis of their susceptibility to reaction with silica and/or fluoride in dilute aqueous solution.

TABLE 2

Sample	% $\text{MgCO}_3$	% Insol. Residue	% of Total Silica Consumed	% of Total Fluoride Consumed
1	27.0	28.0	53	14
2	29.3	16.0	47	17
3	19.8	14.2	41	25
4	19.2	10.8	30	31
5	34.8	10.2	23	46
6	18.4	4.0	11	63
7	1.4	0.04	11	68
8	1.0	0.01	9	72

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The susceptibility to replacement by fluoride was determined as follows. Fifty grams of washed aggregate chips were placed in a polyethylene bottle and equilibrated with 500 ml of a  $1 \times 10^{-2}$  M hydrofluoric acid solution. The fluoride concentration was determined after 48 hours by titrating with thorium nitrate (10). The rate of depletion of fluoride caused by two different rocks is plotted in Figure 2. The first sample is a relatively impure rock (see sample 2 in Table 2) and the second has an insoluble residue content of only 0.5 percent and a magnesium carbonate content of 2.3 percent.

#### SHELL GROWTH IN CONCRETE BARS

Since it was observed that the carbonate rock-silica reaction proceeds at a measurable rate in dilute aqueous solution, attempts were made to "grow" reaction shells on aggregates in experimental concrete bars under laboratory conditions. Forty 2- by 2- by 14-in. bars were prepared in the laboratory of the Iowa State Highway Commission. The cement paste was made in batches of the following size and composition: Cement (Penn Dixie, Type 1) —750 g; Graded Ottawa Sand—

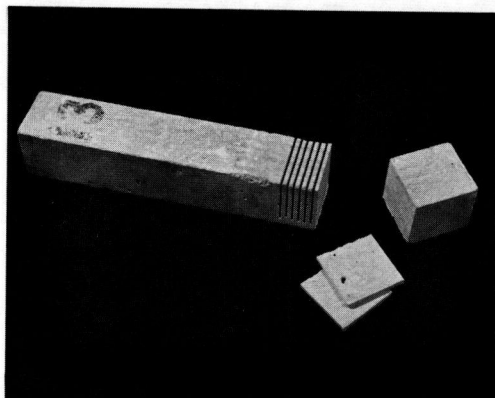


Figure 3. Test bar and sections cut to expose aggregate.

2,063 g; and Water—400 cc $\pm$ 50 cc. Two main types of coarse aggregate, acceptable and unacceptable, differentiated on the basis of service records, were used in these bars. After proper setting and aging for periods up to two months these bars were subjected to one of three different environments:

1. Room temperature with no added moisture.
2. Immersed in distilled water at 120-125 F.
3. Alternate soaking and drying (soaked in distilled water at room temperature for 24 hr and dried at 140 F for 24 hr).

After several weeks of treatment some of the bars were cut into thin wafers to expose the aggregate (Fig. 3). Visible reaction shells had already formed on the unacceptable type in those bars which were kept in environments B or C. These same type rocks developed no shells in environment A. The acceptable aggregate developed

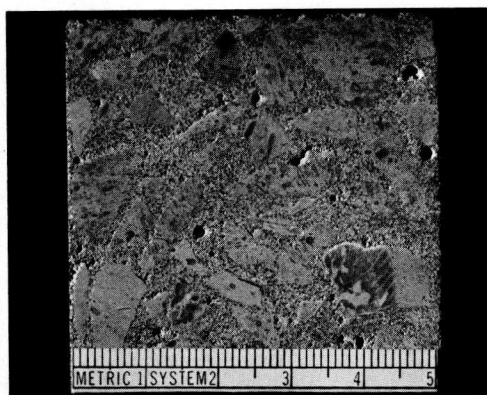


Figure 4.



Figure 5.



Figure 6.

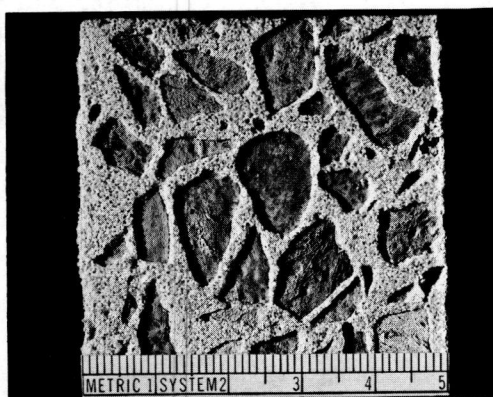


Figure 7.

Figures 4, 5, 6 and 7. Sections taken from test bars made with acceptable aggregate before (top) and after (bottom) residence in environment B. In each case an unetched (left) and an acid-etched section (right) are shown. Illumination is from the left.



no visible shells in either of the three environments. In each case, the presence or absence of the shell was also determined by acid etching of a smooth-cut section of the bar. This was done by immersing the section in several hundred ml of 2 - 3 N hydrochloric acid for an appropriate length of time. In many instances the entire carbonate fragments were silicified rather than just a peripheral rim zone.

Figures 4 through 7 illustrate the appearance of sections of a bar containing acceptable aggregate, before and after being placed in environments A and B. In each case an unetched (left) and an etched (right) surface are shown. Figure 4 shows an unetched section through a bar which was subjected to environment A. Each aggregate fragment is bounded by a thin white line. This line is a result of carbonation of a narrow zone of lime which accumulates at the surface of the aggregate particles before the cement sets. This occurs at the surface of any type of aggregate or other solid object, as can



Figure 8.

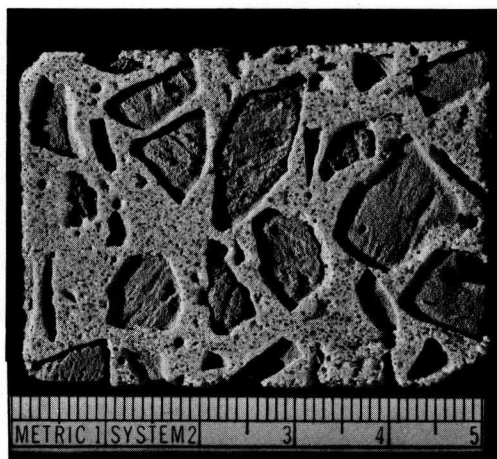


Figure 9.

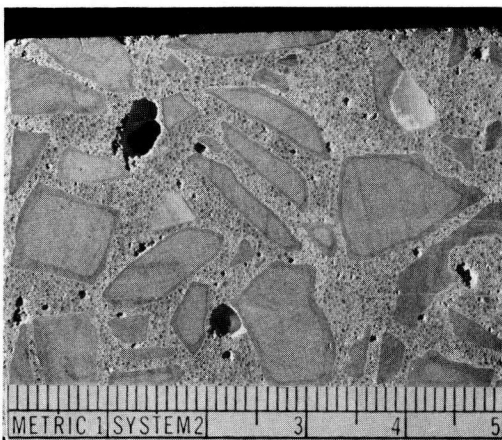


Figure 10.

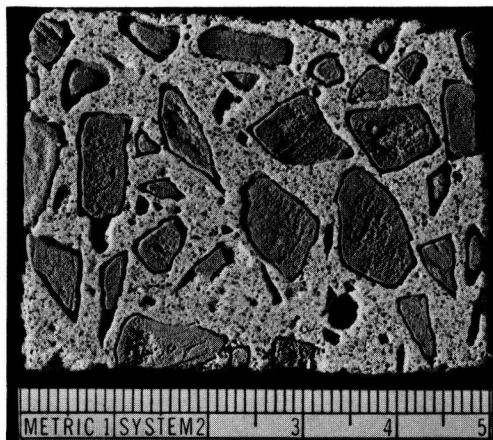


Figure 11.

Figures 8, 9, 10 and 11. Sections taken from test bars made with unacceptable aggregate before (top) and after (bottom) residence in environment B. In each case an unetched (left) and an acid-etched section are shown. Illumination is from the left.

be demonstrated by allowing cement paste to set in a glass container. The lines are more easily seen in Figure 8 because of the darker color of the aggregate. This very thin zone of high carbonate will be subsequently referred to as the "carbonate halo".

Figure 5 is an acid-etched section from the same bar. The aggregate fragments have been deeply "entrenched" by etching and there is no differentiation of zones at the aggregate-cement paste boundary.

Figures 6 and 7 illustrate the same relationship for a companion bar (same aggregate) which was subjected to environment B. Again there are no visible shells and etching does not differentiate any zones at the particle boundary.

Figures 8 through 11 show the results of identical treatment of sections through bars made with unacceptable aggregate. The differences are striking. Although the aggregate in the bar which was kept dry is no different in susceptibility to etching (There is, of course, a slight difference due to the higher percent of acid insoluble impurities but here the concern is with the relationship of the aggregate to the surrounding cement paste, and this is essentially the same.) than the acceptable aggregate in the preceding photo series, a marked difference arises after residence in environment B for 60 days (Fig. 10). In this case visible shells have formed and the entire aggregate particle has been rendered less susceptible to acid attack (Fig. 11).

The deep, narrow "trench" around each of the aggregate particles may be due to the presence of the carbonate halo which originally surrounded the particles. This highly soluble zone allows the acid to penetrate immediately and etch the affected aggregate (that is, the shell zone). The etching in this case would be enhanced by the vigorous evolution of carbon dioxide which would mechanically break up the skeletal, siliceous remains of the rim zone which is quite delicate when saturated. It is not unreasonable to assume that the fine carbonate responsible for the halo would also reside in some of the larger pores of the rock, thereby increasing the effect.

Figures 12 and 13 are close-ups of several of the aggregate particles in Figures 9 and 11, respectively. The black fibers were used to emphasize the relationship of the aggregate to the cement paste in regard to relief. The shadow of the right fiber (Fig. 12, illumination from the lower left) shows the depression of the aggregate particle. The fibers in Figure 13 are essentially horizontal. Figure 13 also clearly shows the entrenched zone around the larger aggregate fragments. The very small fragments such as the one between the two large fragments in this close-up are not resistant to etching. This might be explained by the same mechanism previously postulated to account for the deep entrenched zones around the larger particles, since most of these fragments are not much more than twice as wide as the "trenches".

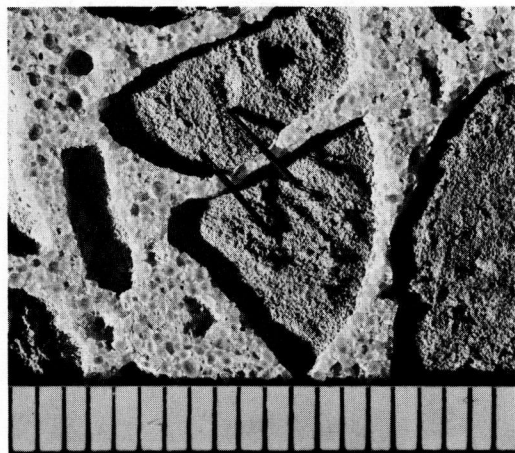


Figure 12. A close-up of a portion of the section shown in Fig. 9. Illumination is from the lower left.

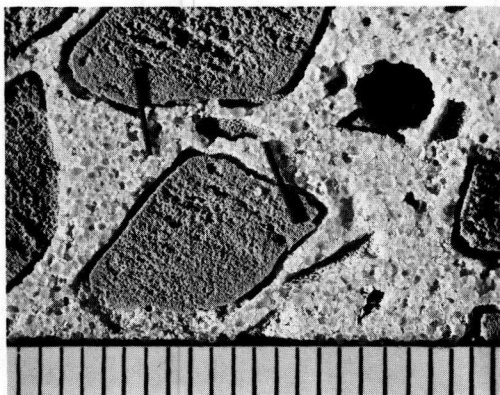


Figure 13. A close-up of a portion of the section shown in Fig. 11. In this case the aggregate fragments are "leached" of calcareous material but a siliceous skeletal structure remains.

The surfaces shown in Figures 9 and 11 were etched side-by-side in the same hydrochloric acid solution (3N) for the same length of time. The acid etched surface of a section taken from the same bar as the section shown in Figure 11, after only 30 days of treatment (as opposed to 60 days), shows clearly that the periphery of the particles is silicified before the interior (Fig. 14).

These photos are not examples of isolated instances; the same decrease in solubility of the unacceptable aggregate fragments occurred in every bar subjected to environments B or C.



Figure 14. An acid-etched section taken from the same test bar as the section shown in Fig. 11, after only 30 days (as opposed to 60) in environment B.

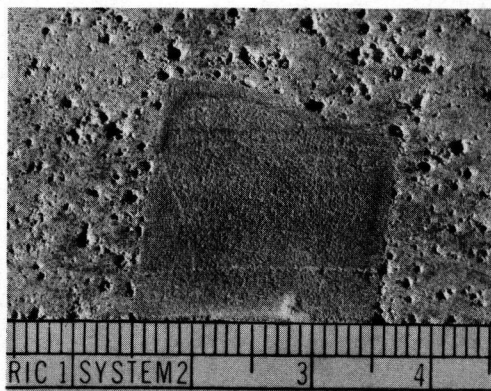


Figure 15.

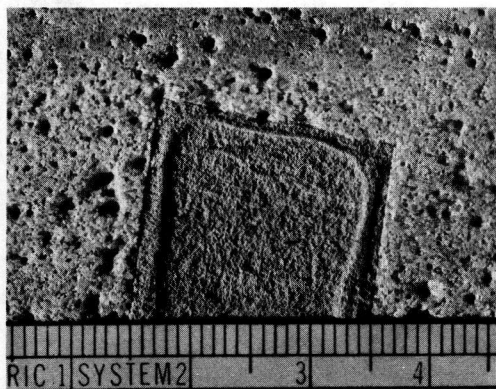


Figure 16.

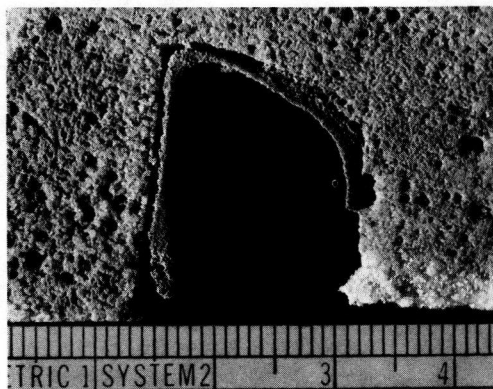


Figure 17.

Figures 15, 16, and 17. Three adjacent sections taken from a test bar containing an aggregate block. Fig. 15, no acid etching; Fig. 16, etched for several minutes in 3N HCl; and, Fig. 17, prolonged etching has completely removed the unsilicified interior portion.



To achieve shell growth on planar surfaces, samples of carbonate rocks were cut into blocks and molded into experimental bars. The bars were then placed in environment B for 30 days after which sections were taken for etching. Figures 15 through 17 show different stages of acid etching of thin wafer sections cut through a single aggregate block. In the most advanced step (Fig. 17) the siliceous shell remains, whereas the unaffected portion has been completely etched away. This spongy-appearing rim zone is quite delicate when saturated but can be handled when dry.

Figure 18 is included to demonstrate that an aggregate particle may lack a visible shell zone and still be affected. The left two-thirds of this specimen also illustrates the fact that shell growth may vary in the same rock. This must be due to a variable within the rock structure since the cement paste is essentially homogeneous. It does not seem likely that this variable is dolomite content since the area of differential shell growth (just below the middle of the left edge of the aggregate block) is replete with dolomite rhombs. It does appear that the most intense shell growth tapers off to the right and corresponds with a slight ridge which can be seen in the etched interior zone.

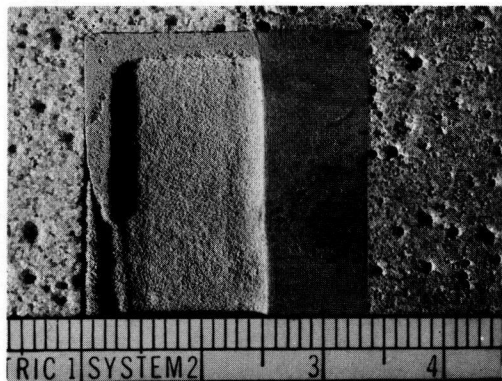


Figure 18. Section of a test bar containing an aggregate block. The left two-thirds has been acid etched to accentuate the shell. Illumination is from the left.

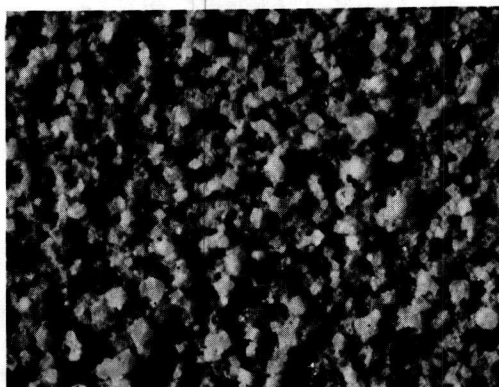


Figure 19. A close-up (x50 magnification) showing the relationship of dolomite rhombs to matrix in the unsilicified interior of the aggregate particle in Fig. 18 after acid etching. Compare with Fig. 21.

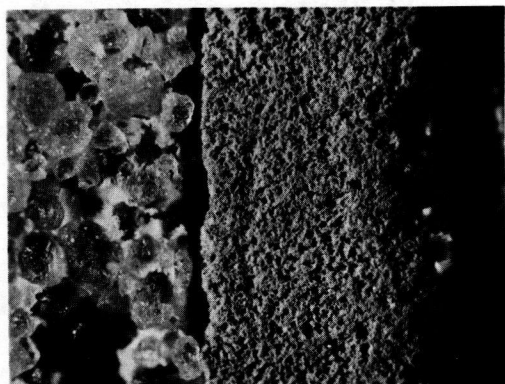


Figure 20. A close-up (x20 magnification) of the acid leached shell zone shown in Fig. 18. On the left is leached cement paste.



Figure 21. A close-up (x60 magnification) showing perfect "casts" of dolomite rhombs which were etched from the silicified shell zone. Compare with Fig. 19.

A closer examination of the etched interior portion of this specimen (the area directly above the numeral 2 on the scale) and of the acid-leached shell zone (upper left edge of the aggregate block) shows an interesting differentiation of dolomite rhombs and "matrix".

A close-up of the etched interior portion (Fig. 19) demonstrates that the matrix (that is, the more calcareous material containing the acid insoluble fraction of the rock) is leached away more readily than the rhombs themselves. This relationship is drastically changed in the shell zone. Figure 20 is a close-up of the acid-leached shell zone in Figure 18. It can be seen that the leached shell is spongy in appearance. A still closer view of the shell (Fig. 21) shows that the holes are actually casts of dolomite rhombs which have been dissolved out of the silicified matrix. These latter figures illustrate that the material between the rhombs is definitely altered as the shell forms, whereas the dolomite rhombs are unaffected.

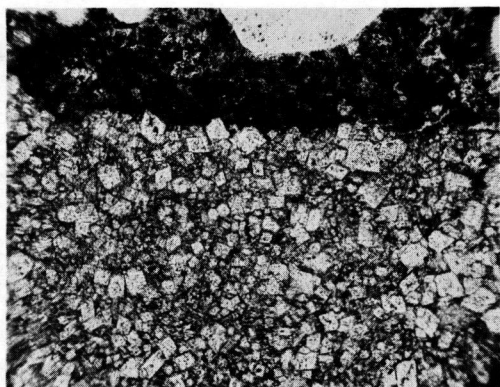


Figure 22. A thin-section view (x100 magnification) of dolomite rhombs in a well developed shell taken from a highway sample. No corrosion of the dolomite is apparent. The dark portion at the top is cement paste.

Figure 22 is a greater magnification of a thin section showing dolomite rhombs in a well developed reaction shell from a highway sample. The dark portion at the top of the photo is cement paste. The lighter field at the bottom is entirely within the shell zone. It is clear that the dolomite rhombs are well defined and not corroded to any marked degree. Hence, this process of silicification is selective. In this case, well organized dolomite rhombs are unaffected while the calcitic matrix is altered.

An example illustrating variability in the degree of silicification is shown in Figures 23 through 26. This series shows stages in the progressive etching of a section cut from a concrete bar containing a block of aggregate which displays three

local variations in lithologic character (Fig. 23). The section was etched by completely immersing it in 3N hydrochloric acid for an appropriate length of time.

The penetration and nature of the shell being formed is influenced by the nature of the host rock. In the upper zone a prominent frontal "wave" precedes the main wave and the relationship between the two is quite consistent. In the narrow middle zone, the penetration is somewhat hindered. This zone is also the most soluble in acid (Fig. 26). In the lower zone the penetration is greater than in either of the latter and the wave fronts are not as prominent. Hence, the same rock unit may exhibit varying degrees of susceptibility to silicification, depending upon its lithologic homogeneity.

Several of the carbonate aggregate blocks were soaked in a  $5 \times 10^{-2}$  M silica solution (pH 12) for two days prior to placing them in a bar in environment B, to determine what effect this would have on subsequent shell growth in concrete. All four surfaces of the block were soaked in the silica solution but only three of them were exposed to contact with the cement paste. This "double treatment" resulted in two separate shells after etching (Fig. 27). The fact that the inner shell is not merely a frontal "wave" as is seen in Figures 24 through 26 was proven by growing a single shell on a fragment of the same rock. Obviously the inner shell was grown in the silica solution since it is connected to the single shell on the lower surface which was exposed to the solution but not to the cement paste. Only the lower three-fourths of the specimen was etched, hence, the double rim on the top surface has not been exposed. It was observed, however, on other wafers cut from the same block. This case alone is a very strong indication that shell growth is due to the introduction of silica. Here one shell was grown in a silica solution and an identical, separate shell was grown by molding the aggregate in a concrete bar and placing the bar in environment B. The relationship between the

single shell on the lower surface and the inner shell on the other surfaces shows that the inner shell first formed at the surface and then migrated inward as the second shell formed.

Although the right surface of the aggregate block in Figure 27 was thickly coated by rubbing a laboratory grease pencil over it prior to any treatment, there is no marked difference in the degree of shell growth.

The sampling of shell zones for chemical analysis is quite tedious. Any practical method of procuring a quantity of a representative sample of these zones and a sample of the adjacent unaffected rock for chemical comparison is open to criticism, since contamination of either portion by the other or by fragments of cement paste and/or fine quartz aggregate would cause serious variations.

The following method was used to circumvent sampling difficulties. Chips of a given aggregate, passing a 6-mesh sieve and retained on an 8-mesh sieve, were washed with distilled water and dried to constant weight at 80 C. The chips were then divided into two portions, one of which was set aside for chemical analysis and the other treated in the manner described below.

Exactly one hundred chips of known dry weight were placed in "ports" of specially molded bars (Fig. 28) and the bars placed in environment B. At intervals up to 60 days the chips were removed with tweezers, counted, rinsed in distilled water, and dried to constant weight at 80 C. Small chips were used so that subsequent shell growth would affect the entire particle, effectively converting each chip to a shell.

The chips of unacceptable aggregate began to gain weight while samples of purer sub-lithographic limestones (acceptable aggregate) lost weight. Curves A and B (Fig. 29) show the weight increase for samples of two different lithologic units during a 60-day period. Samples of these same chips were placed in a basic solution (pH 12) for the same length of time to determine how their weight would be affected. In this case the chips lost weight as shown by curve C (Fig. 29). This same curve would serve as an approximate indication of the average weight loss experienced by chips of acceptable aggregate, that is, relatively pure limestone. This decrease in weight is

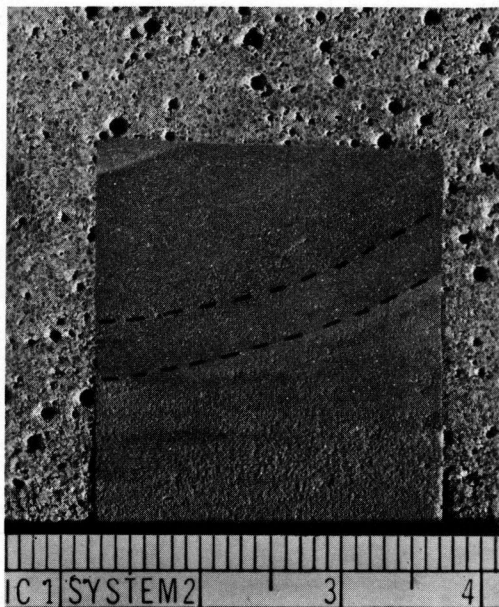


Figure 23.

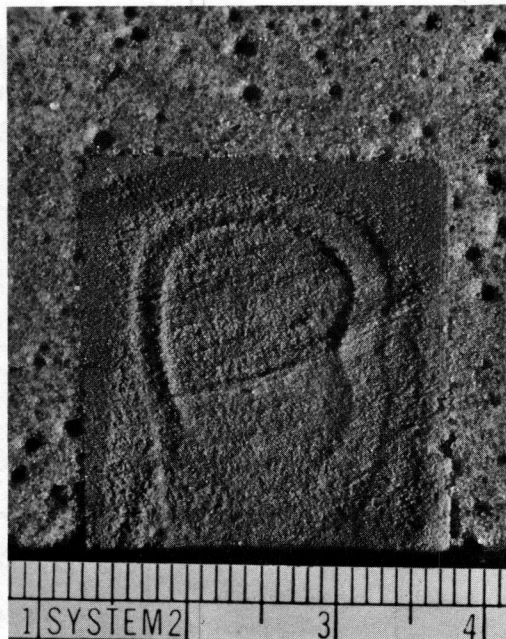


Figure 24.



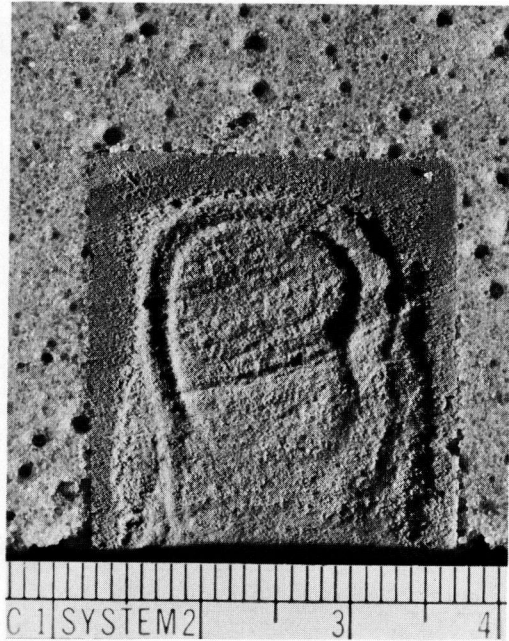


Figure 25.

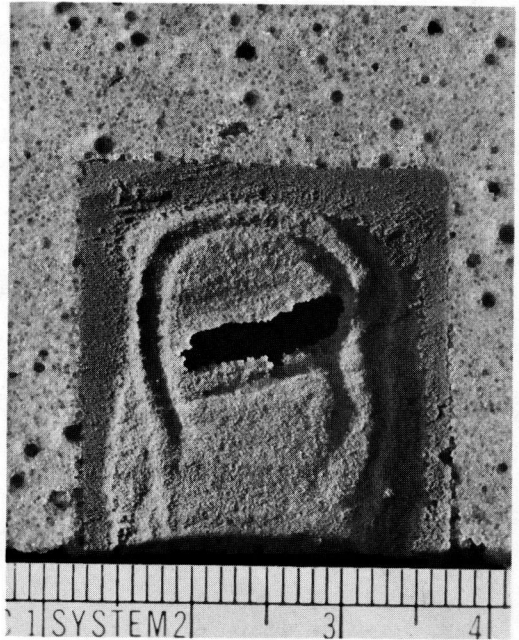


Figure 26.

Figures 23, 24, 25, and 26. Progressive etching of a section exposing an aggregate block of varying lithology in which a shell has been "grown". It is clear that the penetration and nature of the shell varies with the lithologic character of the rock.

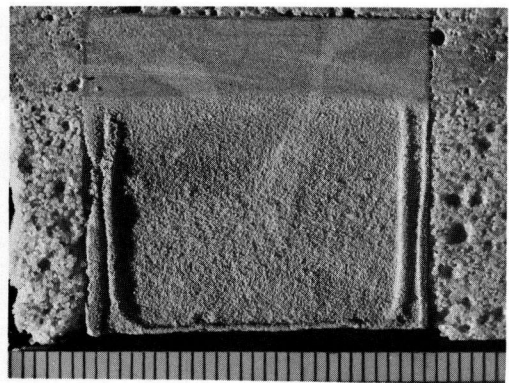


Figure 27. Two separate shells which were formed by first soaking the aggregate block in a silica solution and then molding it into a concrete bar and placing the bar in environment B. Only the lower three-fourths of the specimen gas been acid etched. Illumination is from the left.

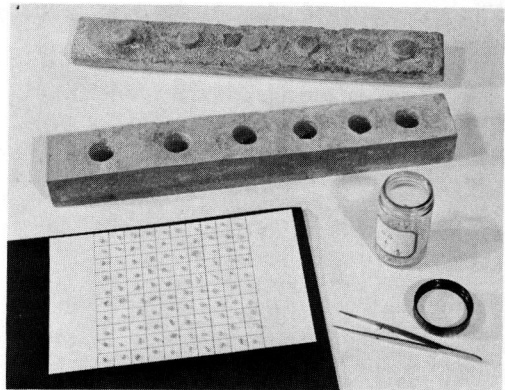


Figure 28. Specially molded experimental bar containing six "ports" in which aggregate chips were placed.

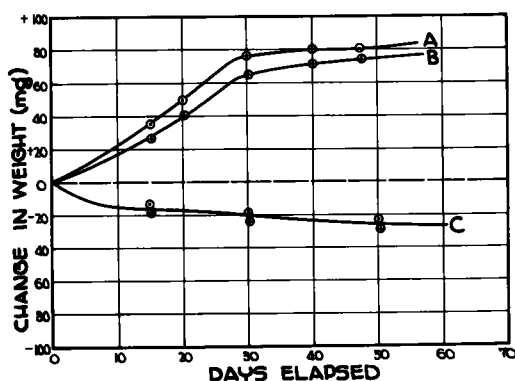


Figure 29. Change in weight of unacceptable aggregates, curves A and B, and acceptable aggregates, curve C after being stored in the ports of a test bar such as is shown in Fig. 28.

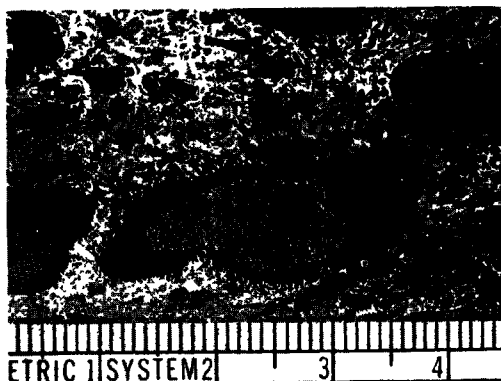


Figure 30. An example of silicification in nature. A section through a fossiliferous chert nodule, exposing a carbonate fragment. See also Fig. 31.

#### A. HOST ROCK

$\text{CaCO}_3$  - 92.1 %

$\text{MgCO}_3$  - 5.6 %

$\text{SiO}_2$  -  $\frac{1.4}{99.1}$  %

#### B RIM ZONE

$\text{CaCO}_3$  - 3.5 %

$\text{MgCO}_3$  - 0.6 %

$\text{SiO}_2$  -  $\frac{94.8}{98.9}$  %

#### C. CHERT

$\text{SiO}_2$  - 98.7 %

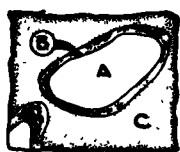


TABLE 3

Sample	% $\text{SiO}_2$ Before	% $\text{SiO}_2$ After
1	7.25	13.20
2	16.25	19.00
3	15.20	19.10
4	16.10	20.25
5	11.30	12.85
6	14.30	16.10
7	10.75	14.50

Figure 31. Chemical analyses of the section shown in Fig. 30.

due to slow leaching of more soluble components of the rock and probably some mechanical loss of very small fragments due to handling. This weight loss accounts for the slight dip in the early portion of curves A and B. In other words, the aggregate chips are being leached of soluble components and taking on silica at the same time, the latter process dominating.

Chemical analyses of seven samples of unacceptable aggregate chips before and after this treatment show increase in silica content (Table 3).

In this case the only possible source of silica other than the cement paste is the fine quartz aggregate in the cement paste. To check this possibility, aggregate chips were placed in vials with neat cement paste and distilled water at 125 F. These chips gained weight at rates and quantities comparable to the gain shown in curves A and B (Fig. 29). If identical samples of chips were kept in vials with fine quartz aggregate and basic solution maintained at pH 12 and 125 F they lost weight at rates and degrees comparable to those represented by curve C.

## CONCLUSIONS

It has been demonstrated that siliceous reaction shells can be experimentally "grown" in the types of carbonate aggregate which display such shells in samples of distressed concrete whereas the same conditions will not cause shells to form in fragments of acceptable aggregate. If one were to make an approximate, hypothetical cal-

culuation assuming that 40 percent of the volume of concrete is coarse aggregate of 1-in. cubes, and further assuming that this aggregate is silicified to a depth of  $\frac{1}{8}$  in. and to a degree indicated by an average of the results in Table 3, he would find that approximately 5 to 10 percent of the silica present in average neat cement paste has been stabilized in the carbonate aggregate.

The exact mechanism of shell growth can only be postulated at this time. Bisque and Lemish (1) showed that the effective porosity of the rim shell is markedly decreased as compared to the unaffected aggregate or host rock. This would suggest that mere pore-space filling is involved, but there are also indications that a two-way exchange occurs to some extent. Lemish et al. (7) show that the increased birefringence of the cement paste adjacent to rimmed aggregates as compared to the lack of such birefringence in sound cement paste and interpret this to indicate that the paste has been "carbonated." While studying shell growth in aqueous solution, Bisque and Lemish noted that in some instances depletion of silica concentration was accompanied by a yellowing of the silica solution. The intensity of the "yellowing", as determined by reading the optical absorbency of the solutions at  $4,000 \text{ \AA}$  was found to depend on the concentration of the silica in solution when the pH was kept constant. The yellow color was attributed to the introduction of iron since the amount of iron in solution and/or suspension was found to be proportional to the intensity of the color. The exact nature of the species involved at this pH is not known but there are indications in the chemical literature that iron is complexed by silicate at high pH. Fortune and Mellon (3) found that silicate interfered with the formation of the iron-O-phenanthroline complex at pH values above 4.5. The amount of iron freed from the rock was found to be proportional to the concentration of silica in the solution and hence proportional to the degree of silicification.

A two-way exchange of substances, as indicated by the above observations, would be analogous to a rather common occurrence in nature which geologists refer to as "replacement." An example of replacement of a carbonate particle by silica in nature is shown in Figure 30. In this case a carbonate fragment inbedded in a chert nodule has been partially replaced by silica, resulting in a shell very similar in appearance to shells observed in distressed concrete. Chemical analyses of each of the respective zones are given in Figure 31.

The authors feel that the evidence cited indicates that the clay fraction (1) of the acid insoluble portion of these rocks is responsible for their susceptibility to the type of silicification described. The three-dimensional siliceous network which remains after leaching of all calcareous material from a sample of shell material is a strong indication that clay is involved.

It is extremely difficult to postulate a mechanism for the formation of such a network unless one appeals to the clay particles distributed throughout these rocks. (In thin sections the clay particles appear as well disseminated semi-opaque specks throughout the calcitic matrix.) It is not possible that the small increase in silica content in the shell zone (Table 3) is alone responsible for the insoluble, spongy-appearing material which remains after acid leaching of all calcareous material (Figs. 20 and 21). The weight of this siliceous skeleton is often more than three times as great as the weight of secondary or introduced silica which caused its formation. In addition the skeleton contains appreciable aluminum (Table 4). The weight relationship was demonstrated by first silicifying a piece of aggregate, leaching it with acid, and weighing the dried siliceous skeleton which remains. This weight was then compared with the weight of silica which was added to the rock (Table 4 See also Table 3).

It would require a relatively small amount of silica, however, to join or tie together the finely divided clay particles in the rock and thus fabricate this network. Although they have been subjected to the same conditions, aggregates which lack clay have not grown siliceous shells in the laboratory.

The type of reactivity postulated above would not involve a two-way exchange of material as was necessary for the type of silicification shown in Figures 30 and 31. As previously noted, it is entirely possible that a true replacement of carbonate minerals by silica also occurs to some extent in the reaction shells found in concrete. This latter process, however, may take place at a much slower rate.

TABLE 4

Sample (See Table 3)	Wt. % SiO <sub>2</sub> "Added"	Wt. % Siliceous Skeleton After Leaching <sup>a</sup>	Wt. % Al <sub>2</sub> O <sub>3</sub> in Skeleton
2	3.25	10.7	14.0
4	4.15	11.8	9.0
6	1.80	4.9	21.0

<sup>a</sup> Because of difficulty in preventing loss of some siliceous skeleton during leaching and drying, differences may be greater than is indicated by columns 2 and 3.

Another theory, less favored by the authors, is that the clay material may not be directly involved in the silicification but may act as a catalyst. This effect might be accomplished by disruption of orderly carbonate crystal lattices, thereby providing a large effective surface area and/or an abundance of reactive sites. The formation of an acid insoluble siliceous network is not easily reconciled with this theory.

The reason for the definite separation of the two shells is not clear, but the same phenomena occurred in all of the blocks treated in this fashion. The separation may be due to a mechanism similar to the type, or types, responsible for rhythmic precipitation which is associated with the formation of "Liesegang rings" in nature (5). The frontal "wave" seen in Figures 24 through 26 is definitely due to rhythmic precipitation since the source of the migrating species, silica, was constant and uninterrupted.

### SUMMARY

In studying concrete made with carbonate aggregate, the authors have defined a type of silica activity which they believe is: (a) distinct from the alkali-aggregate reaction; (b) deleterious to the stability of cement paste; and (c) limited to only certain types of carbonate aggregates. Reaction shells can be grown in certain aggregates under controlled laboratory conditions. If the formation of reaction shells is considered to be a definitive characteristic of potentially deleterious carbonate aggregates, a relatively simple means of identifying these aggregates has been defined.

### ACKNOWLEDGMENTS

This report is the result of a project sponsored by the Iowa Highway Research Board with funds from the Iowa State Highway Commission to study the suitability of carbonate rocks for aggregate in concrete. Special thanks are due the late Bert Myers, Chief Materials Engineer; Mark Morris, Director of Research; and Theodore Welp, Chief Geologist.

C. V. Banks, Department of Chemistry, Iowa State College, gave advice on analytical procedures. C. J. Roy, Chairman, and others of the staff of the Geology Department are thanked for their interest and cooperation.

Lou Facto, head of the photographic laboratory of the Agricultural Experiment Station of Iowa State College, took the photographs.

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