

# Compositional Variations Associated with Carbonate Aggregate Reactions

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Changes in the composition of aggregates and cement pastes were studied by placing cubes of various aggregates in cement paste bars and reacting them in a water bath at 130 F for a 3-mo period. Chemical and X-ray analyses were made on samples taken at specified intervals across the aggregate into the cement paste. The data indicate that much of the silica in the shell zone is locally derived from breakdown of quartz. Silica can migrate out of the rock into the cement paste or farther back into the rock. Dedolomitization is a concurrent reaction.

Silica migration was postulated to represent an equilibrium reaction controlled by the relative concentration of available silica in adjacent cement and aggregate and the local pH environment.

The results indicate that carbonate aggregate reactions represent an attempt of aggregates to come into equilibrium with the high pH environment of concrete. Silica migration and dedolomitization occur concurrently. Released calcium could react to form calcium carbonate. Silica in the shell zones can be locally derived from the aggregate itself when a cement paste medium is used for the reaction. Cement pastes are not a source of silica but may provide calcium and high pH environment.

• WITH THE recognition of the reactivity of some carbonate rocks used as coarse aggregate in concrete (1, 2, 3) a considerable amount of research has been conducted on such rock and its reaction in Iowa (1, 2, 4, 5, 6, 7) and elsewhere (3, 8, 9). To date most of the effort has been concentrated in an attempt to understand the nature of the reaction. Such knowledge is necessary before a causal relationship can be definitely established between deleterious behavior and carbonate aggregate reactions in concrete.

The Iowa State Highway Commission was able to correlate the poor service record of certain highways to the carbonate aggregates obtained from some quarries, notably the LeGrand and Glory. Past work which has been concentrated on intensive study of the Glory aggregate indicated the rock was an argillaceous dolomite with relatively high insoluble residue which reacted in highway concrete to form "reaction shells." Such concrete was generally characterized by progressive cracking, spalling away from joints, general weakening, and a soft carbonated matrix. Bisque (2) showed these reaction shells in distressed concrete were silicified. In later laboratory study (4), chips of deleterious aggregate were silicified in mortar bars. No alkali accompanied the silica introduced from the mortar bar. At this point it was evident that silica present in the reaction shells came from an outside source, and it was postulated (5) that cement paste could be a source of silica because no evidence of the reactivity

of the fine aggregate was observed during the experiments. The cement paste is no longer considered a source of silica migrating into reaction shells for reasons presented later. The silica is considered to be locally derived from the insoluble residue of the carbonate aggregate itself or possibly from the fine aggregate in the concrete matrix.

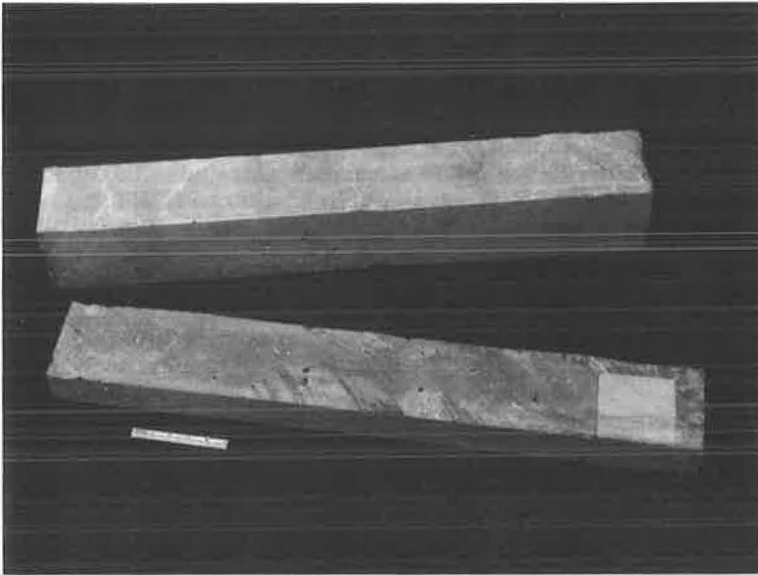


Figure 1. Samples of 2- by 2- by 14-in. cement paste bars: whole bar (upper) and bar cut in half lengthwise showing embedded carbonate aggregate (lower).

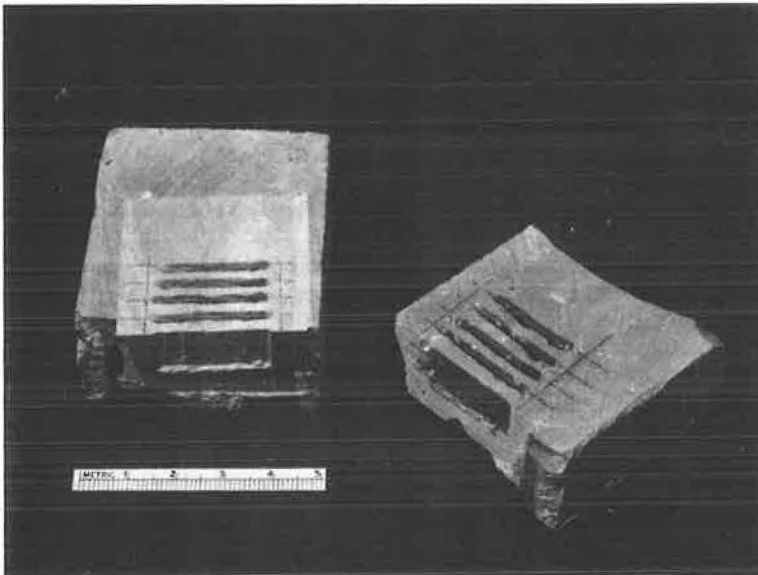


Figure 2. Segments showing spacing of samples in aggregate (left) and in cement paste (right).

The first evidence of the reaction effect on concrete was found when concrete bars made from Glory aggregate and reacted in the laboratory showed no increase in compressive strength (5). Bars made from aggregates with a good service record and reacted at the same time and under the same conditions demonstrated a 50 percent increase in compressive strength.

At this stage of the investigation a more detailed program of research was undertaken with the objective of learning more concerning the nature and mechanism of the reaction. The objective was approached through a study of compositional variations of carbonate aggregates in carbonate aggregate-cement paste reactions.

#### COMPOSITIONAL VARIATIONS OF CARBONATE AGGREGATES IN CEMENT PASTE

The effect of the reaction on the various components of the aggregate (carbonate minerals, quartz, clay, etc.) was investigated through an approach in which the compositional variations in aggregate and cement resulting from aggregate-cement paste reactions were studied.

Cubes of various carbonate aggregate approximately  $1\frac{3}{4}$  in. on a side were embedded in 2- by 2- by 14-in. bars of cement paste. The cement paste bars were made from Type I cement containing 0.52 percent equivalent  $\text{Na}_2\text{O}$  by mixing 2,500 g of cement with 600 ml of water and curing for 48 hr in the moist room. The bars were then treated by soaking in distilled water at 55 C for a period of 3 mo. After treatment the bars were cut in half lengthwise and samples were taken by means of a dental drill at 5 mm intervals from the cement paste across the interface into the aggregate (Figs. 1 and 2).  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  were determined by versene titrametric methods.

TABLE 1  
CHEMICAL ANALYSES OF CEMENT PASTE AND ADJACENT AGGREGATES

Specimen	Distance from Interface (mm)	Cement Paste (%)					Distance from Interface (mm)	Carbonate Aggregate (%)				
		$\text{SiO}_2$	$\text{CaO}$	$\text{MgO}$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$		$\text{SiO}_2$	$\text{CaO}$	$\text{MgO}$	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$
Newton 19	0	20.80	55.2	7.0	1.27	4.32	0-25	8.55	30.2	21.5	1.10	2.16
	5	19.35	48.4	7.0	2.53	3.06	2.5-5	8.60	29.1	17.9	0.84	1.95
	10	18.90	47.0	7.6	2.27	3.08	5-7.5	13.50	29.7	18.2	0.97	1.84
	15	19.30	47.4	7.7	2.16	3.78	7.5-10	-	28.7	17.8	0.78	2.02
	20	19.25	46.8	8.0	2.13	3.88	10-12.5	10.70	28.13	17.9	0.72	2.16
	40	20.20	50.5	5.4	2.35	4.00	12.5-15	-	29.8	16.7	1.00	1.88
	60	19.85	50.0	6.5	2.48	3.87	15-17.5	-	24.7	19.8	0.35	1.99
							17.5-20	-	28.9	17.8	0.77	1.99
Newton 6A	0	9.25	30.5	19.4	-	-	20-22.5	-	28.6	17.8	0.76	2.10
	5	21.60	50.8	2.9	-	-	0-2.5	10.40	52.4	3.4	-	-
	10	18.45	44.9	7.6	-	-	2.5-5	12.55	52.6	3.2	-	-
	15	18.35	46.1	3.6	-	-	5-8	9.23	49.0	5.7	-	-
	20	18.15	48.2	5.7	-	-	15	10.80	49.6	5.1	-	-
	40	19.30	48.2	5.6	-	-	20	11.20	49.2	5.8	-	-
Kenwood C	0	18.5	53.2	2.10	2.94	4.24	0	15.9	34.6	9.70	0.89	1.94
	5	17.6	53.9	2.33	3.00	3.61	5	15.0	36.0	9.60	0.95	1.86
	10	18.2	53.4	2.75	3.16	4.23	15	19.0	31.9	11.30	1.30	1.46
	15	18.1	50.8	4.10	2.60	4.26	20	19.7	30.6	11.60	1.10	2.01
	20	18.4	52.1	3.55	2.66	4.58						
Glory 9	0	17.90	57.4	3.37	-	-	0	8.92	38.1	11.80	-	-
	5	18.95	51.6	5.66	-	-	5	11.02	37.1	11.90	-	-
	10	18.70	51.3	6.24	-	-	10	9.84	35.3	12.90	-	-
	20	18.30	52.9	4.90	-	-	20	10.01	36.0	13.30	-	-
Alite +	0	21.7	60.3	0.43	-	-	0	8.96	39.8	10.4	-	-
Glory 11	5	20.7	61.0	0.76	-	-	5	8.95	38.9	10.1	-	-
	20	20.9	61.0	0.81	-	-	20	9.17	39.2	9.3	0.89	1.13
Belite +	0	29.2	55.6	1.00	-	-	0	9.5	33.6	12.4	-	-
Glory 11	5	29.1	56.2	1.00	-	-	5	9.3	33.2	13.1	-	-
	10	29.1	56.7	0.98	-	-	10	9.2	32.4	14.1	-	-
	15	29.2	56.8	0.95	-	-	15	9.5	32.1	14.5	-	-

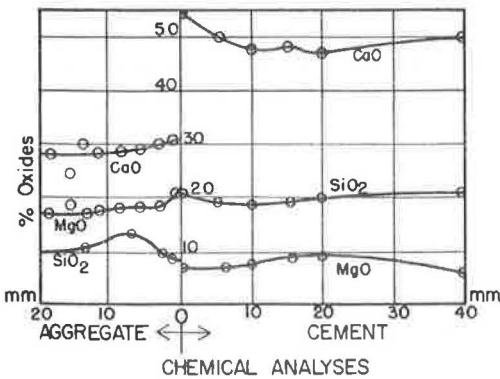


Figure 3. Compositional variations for Newton 19 bar.

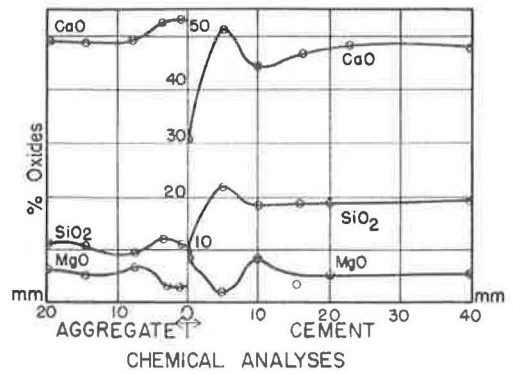


Figure 4. Compositional variations for Newton 6A bar.

Silica was determined by the double dehydration method. Before chemical analyses, semiquantitative X-ray studies were made to determine the mineral or compound content of the aggregate and cement paste, respectively, on the basis of the relative X-ray diffraction peak heights obtained from strip chart recordings of a Norelco X-ray diffractometer. To test the effect of the reaction on the constituents of cement, two cubes of the same reactive aggregate were reacted at pH 12 in bars made from the principal silicate compounds of portland cement, impure alite, and impure belite under the same conditions as the Type I cement paste bars, and sampled accordingly. (The alite and belite were made according to a formula and instructions supplied by L. E.

Copeland of PCA Laboratories. A pH 12 environment in the water bath was maintained by adding NaOH solution.)

The aggregates used were argillaceous dolomitic types which had poor service records or did not pass present acceptance tests of the Iowa State Highway Commission (based essentially on the abrasion loss and durability as related to a water-alcohol freezing and thawing test at Standard Specifications of Iowa State Highway Commission, 1960, pp. 520-521). The Newton 19 and Newton 6A specimens were argillaceous dolomitic limestones from the Coralville member of the Devonian Cedar Valley formation. The Glory 9 and 11 specimens were argillaceous dolomitic limestones from the Rapid member of the Cedar Valley formation. The Kenwood C specimen was an argillaceous calcitic dolomite with a high silica-rich insoluble residue (14 percent) from the Kenwood member of the Devonian Wapsipinicon formation and was the only specimen in which expansion during treatment occurred to the point of cracking the surrounding cement paste.

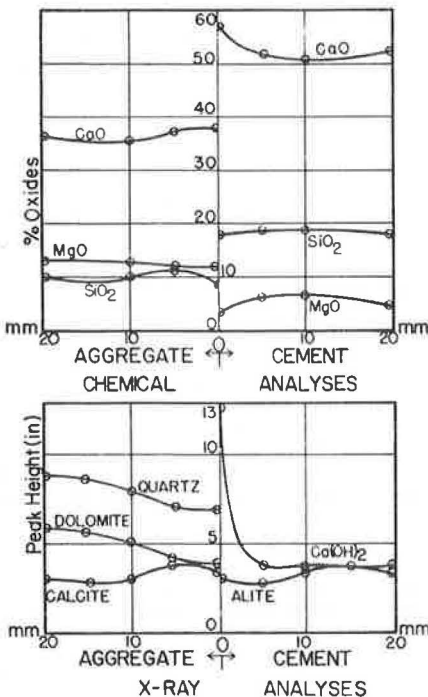


Figure 5. Compositional variations for Glory 9 bar.

#### Analysis of Data

The data are presented in Table 1 and



Figures 3 through 8. Although the experimental approach, nature of the sampling, and procedures employed are such that the study is essentially a reconnaissance approach, the results indicate some significant trends regarding aggregate reactions. The data presented and subsequent interpretations are based on the following assumptions:

1. The aggregate and cement are homogeneous in composition before reaction.
2. The central part of the cubes was least affected by the reaction.
3. The data represent the extent of reaction at the time when the bars were removed from their reaction environment.

The variations in silica content shown in Figs. 3, 4, 6, and 7 are summarized in Fig. 8. In the Newton 19, 6A, and Glory 9 bars (Fig. 8) silica follows a similar pattern in the shell zone interval of 0 to 10 mm from the interface. The silica shows an apparent increase in this zone with the largest amount of silica generally about 5 mm from the interface, whereas at the interface no increase or a slight decrease in silica is indicated. In contrast, the Kenwood C shows a general decrease in silica content throughout the shell zone interval. In the hydrated cement paste, the silica shows variable trends with slight increases at the interface for the Newton 19 and Kenwood C and decrease in the Newton 6A and Glory 9. The Glory 11 aggregate reacted with the hydrated alite and belite (Fig. 7 and lower part of Fig. 8) shows a slight decrease in silica at the interface and a corresponding increase on the cement paste side.

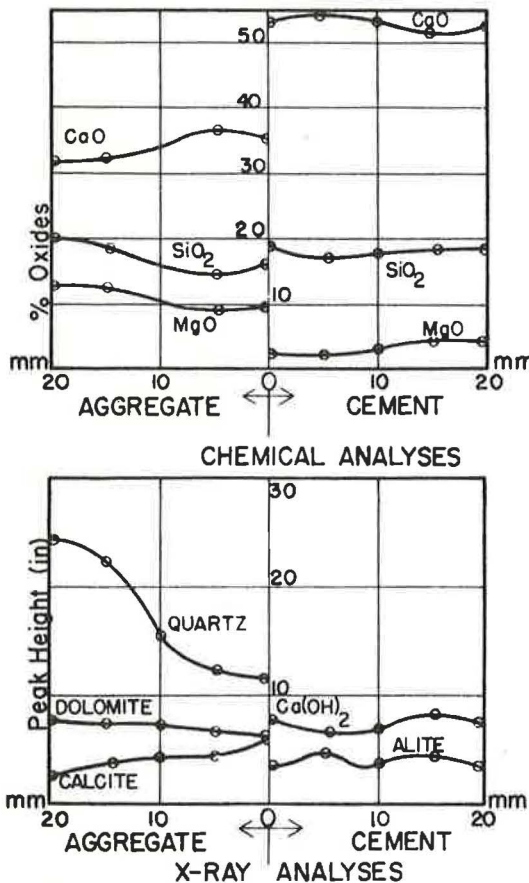


Figure 6. Compositional variations for Kenwood C bar.

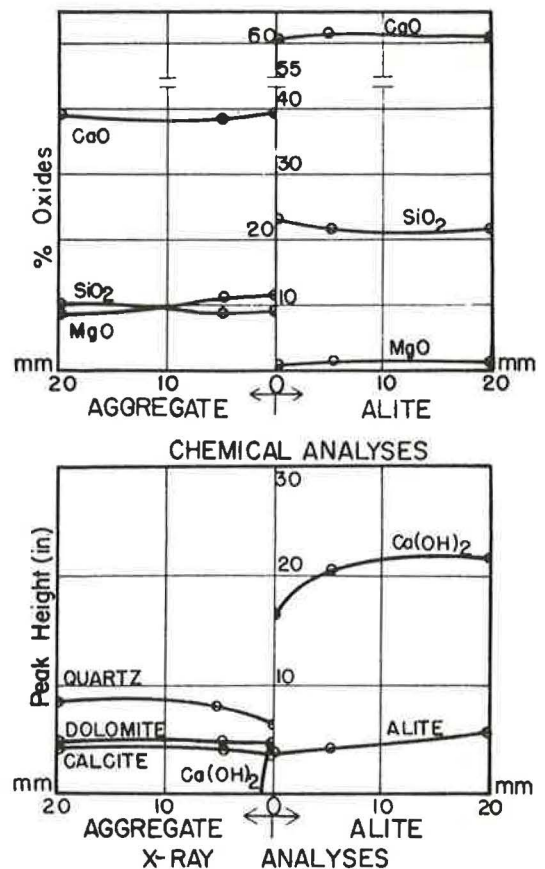


Figure 7. Compositional variations for Glory 11-alite bar.

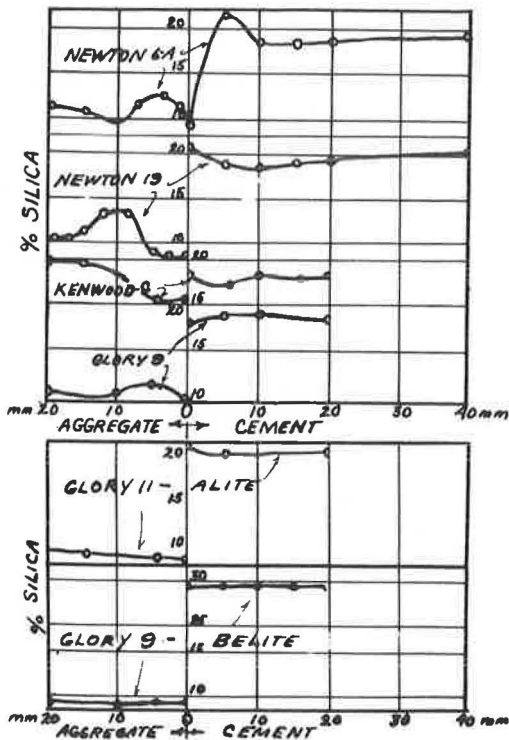


Figure 8. Summary of silica variations.

dedolomitization or introduced from the cement paste as  $\text{Ca}(\text{OH})_2$  (Fig. 7), with  $\text{CO}_3$  made available through dedolomitization.

The chemical and X-ray data indicate quartz is definitely decreased in the shell zone and must be considered a major source for silica. The quartz is part of the insoluble residue and is probably in a finely divided state. The variable behavior of silica which shows a decrease throughout the reaction zone in the Kenwood C and Glory 11 aggregate and a slight increase at about 5 mm from the interface of the other three aggregates, indicates that local quartz-derived silica can migrate either out of or farther into the rock.

To account for these observations it was initially postulated that silica migration is related to the pH environment and moves in a direction to establish equilibrium. A pH gradient was believed to exist (11) and migration direction of silica will depend on the relative amount of locally available silica on either side of the interface, and movement occurs in an attempt to establish equilibrium.

After this postulation was made additional research brought forth some pertinent

$\text{CaO}$  shows a general increase in reaction zone interval for all the aggregates and variable behavior in the cement paste.  $\text{MgO}$  in general decreases in aggregates as the interface is approached.  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , where determined, show minor variations and nothing systematic.

The semiquantitative X-ray data in Figs. 5, 6, and 7 show that the quartz content decreases in the reaction zone of the aggregates. Calcite shows an increase in the reaction zone and dolomite a corresponding decrease. The cement compounds represented by hydrated alite are somewhat variable and the X-ray patterns show evidence of some disorder in the cement paste near the aggregate.  $\text{Ca}(\text{OH})_2$  was found in the Glory 11 aggregate.

#### Interpretation of Results

The chemical evidence for  $\text{CaO}$  and  $\text{MgO}$  and X-ray data for the carbonate minerals show that dolomite appears to be breaking down in the shell zone. This is a concurrent dedolomitization reaction. The calcite increase near the interface may be an apparent effect of the relative decrease in dolomite. It may also reflect formation of some new calcite through the combination of calcium released during

TABLE 2

#### WATER SOLUBLE COMPONENTS OF CEMENT AFTER ONE YEAR AT 25 C

Alkali Content	Silicon (mg)	Calcium (mg)	Magnesium (mg)	pH
High	0.00	3.34	0.071	11.9
Medium	0.00	4.05	0.062	12.0
Low	0.00	4.53	0.052	11.9

information regarding the pH gradient and cement paste as a silica source. These data supplement the interpretation of the compositional variation data.

Hiltrop (11) demonstrated the presence of a pH gradient across the interface in a relatively simple experiment in which a block of Kenwood C rock 2 by  $3\frac{1}{2}$  by 3 in. was embedded within a larger cement paste block so that the rock surface (3 by  $3\frac{1}{2}$  in.) was exposed. Holes  $\frac{3}{16}$  in. in diameter were drilled in the rock and cement paste at various distances from the interface. The holes were stoppered with corks and the block was set in distilled water kept at room temperature at such a depth that the water level came within  $\frac{1}{8}$  in. of the surface of the block. After a period of two weeks water had migrated into the holes in the cement but those in the carbonate rock were dry. The ports were then filled with distilled water and the pH was checked periodically. The equilibrium pH was found to vary from 12 in the cement paste to 9 in the rock at about 5 mm from the interface.

The experiment indicated that a pH gradient exists and demonstrates that hydroxyl ions migrate from the cement paste into the rock because the rock is a poorer source of hydroxyl ions.

Hydrated cement paste was found to be a poor source of silica because of evidence obtained from several areas. Werner (12) determined this by placing 200-g samples of high, medium, and low alkali cements in polyethylene bottles and adding 200 ml of distilled water to each bottle. The samples were allowed to stand at room temperature (23 to 25 C) for one year. The solutions were then analyzed for silicon, calcium, and magnesium, with the results as shown in Table 2.

These additional data indicate that when aggregates are reacted with cement pastes the aggregates are the major source of silica available for migration and the cement paste is the source of the hydroxyl ions which provide the environment for reaction and migration. In re-examining the earlier data on compositional variations, the conditions are such that one would expect silica to migrate from the rock into the cement paste. Such is the case with the Kenwood C and Glory 11. In other aggregates, however, some of the locally derived silica apparently moves farther into the rock leaving a narrow silica deficient zone immediately adjacent to the interface. Migration in this direction, though in response to local conditions, appears to indicate a difference in the adjustment of some rocks to a hydroxyl-rich environment. The complexities of shell formation indicate more research is needed to account for variations in different shells.

An important observation derived from the knowledge of the variable behavior of silica in shell zones is that the presence of a silicified reaction zone in the periphery of an aggregate should not be interpreted as an increase or decrease of the silica content of the shell zone. It does however indicate the presence of either amorphous silica or some silicate compound. Werner's (12) research on these reactions at higher temperatures indicates that mono-calcium silicate hydrates can form as a result of the reaction.

## CONCLUSIONS

The compositional variations associated with the carbonate aggregate-cement paste reactions indicate that the reaction is essentially an attempt of the aggregate to come into equilibrium with the higher pH environment produced by the hydrated cement paste. In experiments with cement paste bars, the silica in the shell zones is locally derived from quartz present in the aggregate and it appears to migrate in the direction required to maintain equilibrium according to the local pH environment. Dedolomitization and possibly an increase in new calcite (calcitization) occurs as a concurrent reaction. Cement pastes are stable and are not considered the source of silica found in the shell zone.

The preceding conclusions are valid for the data and conditions described in this report. The conclusions regarding migration of silica from the aggregate into the cement paste are valid only when cement paste is used to provide the reaction environment. Work by Bisque (2) on aggregate chips in portland cement mortar bars and current research indicate conclusively that silica migrates from the mortar into the aggregate.



## ACKNOWLEDGMENTS

Most of the data in this paper came from thesis research conducted at Iowa State University and sponsored by the Iowa State Highway Commission. Harwood (10) did the study on compositional variations of carbonate aggregate in cement paste. Hiltrop (11) measured pH changes associated with the reaction, and Werner (12) measured the water soluble components in cement. Lemish directed the research and is responsible for writing this paper.

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