

Effect of Illitic Clay on Chemical Stability of Carbonate Aggregates

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This report is related to two previous (3, 5) publications by the authors. The reports are a result of studies aimed at defining the type of chemical reactivity which results in the growth of reaction shells in certain carbonate aggregates. Studies to date have supported the postulation that the clay fraction of these rocks makes them susceptible to this type of reactivity, due to the fact that the clay particles serve to stabilize soluble silicon (the exact ionic species involved are not known; that is, SiO_4^{-4} , $\text{Si}_2\text{O}_7^{-6}$, etc.) and upset equilibria which would normally exist in concrete. The net effect is the formation of a silicon-rich shell around the periphery of the aggregate particle and concomitant removal of silicon from the cement paste.

The present report summarizes additional experimental demonstrations of the fact that the illitic clay fraction of these carbonate aggregates serves to react with silicon in a manner which is distinct from the processes involved in the "alkali-aggregate reaction." Flame photometric analyses of aggregate particles for sodium and potassium were made before and after shell growth, demonstrating that the soda and potash content of the peripheral zone was not increased.

Reaction shells were caused to form in concrete bars under controlled conditions. Similar bars made with acceptable carbonate aggregate were subjected to the same conditions for comparison. Length changes were measured and compressive strength tests were run on both "treated" and "untreated" bars. It was shown that the growth of prominent reaction shells throughout the concrete was not accompanied by excessive expansion of the bars. Preliminary tests indicate that the increase in compressive strength which normally accompanies hydration is definitely diminished when shell growth occurs in the concrete.

● CERTAIN CARBONATE AGGREGATES from quarries in northeastern Iowa have proved to be chemically unstable in portland cement paste. This instability ultimately results in the formation of a siliceous shell in the aggregate particles. The observation that this shell growth is associated with premature deterioration of the concrete prompted studies of the chemical and physical characteristics of aggregates from this area (3, 8, 5, 6, 7).

These studies have demonstrated that the carbonate rocks which undergo this silicification are characterized by a high percentage of acid insoluble components. Further, it was postulated that the clay fraction of the acid-insoluble material is directly involved in the stabilization and retention of silicon which would normally exist in equilibrium with components of the cement paste (5). This latter postulation was supported by photomicrographs and data which demonstrated that the reaction shell which results from this type of silicification contains a three-dimensional siliceous "skeleton" which can be separated from the carbonate minerals by acid leaching and that the structure of the skeleton includes in its make-up an amount of silicon in excess of that which was

stabilized; that is, introduced, to cause it to form. In the light of these observations, it was postulated that the introduced silicon served to combine, or in effect "tie together", some siliceous component within the rock. The presence of an appreciable amount of aluminum in the skeleton was taken to indicate that the siliceous component involved is the clay fraction of the acid insoluble material. Discussion of the nature of this clay fraction and results of chemical analyses are included in another manuscript (4).

The purpose of this paper is to present new data which supplements the aforementioned research on the silicification of carbonate aggregates in concrete and concerns: (a) the relationship of sodium and potassium to shell growth (b) the effect of the reaction on the expansion and strength of concrete bars, and (c) the role of illitic clay.

Chemical analyses of both acceptable- and unacceptable-type carbonate aggregates (that is, acceptability based on actual service records) were made before and after equilibration with concrete in distilled water¹ to determine whether the reaction which causes the formation of shells introduces any soda or potash into the aggregate particles. The results of these analyses are given in Table 1. Soda and potash were determined flame photometrically. The values for potash were consistently less than ten parts per million in both the original and equilibrated aggregates. These data indicate that the amount of soda and potash in the shell zone does not increase as silicon is introduced. Powers and Steinour (11) discuss chemical analyses of samples of siliceous gels taken from various concrete structures affected by the alkali-aggregate reaction. These results demonstrate that such gels contain from 6 to 26 percent soda and potash, soda predominating. The siliceous shell, therefore, is definitely distinct in chemical character from the type of siliceous gel commonly found in concrete which has been weakened by the alkali-aggregate reaction.

For further comparison with the effects of the alkali-aggregate reaction which normally causes expansion of concrete, it was felt that the length changes of experimental bars should be measured while they were subjected to conditions which would cause shell growth. Twenty-eight concrete bars (2 by 2 by 14 in.) containing either acceptable- or unacceptable-type aggregates were prepared.² One-half of each type was subjected to one of the following environments for four months:

Environment A—room temperature and humidity.

Environment C—alternate soaking and drying
(soaked in distilled water at room
temperature for 24 hours and
dried at 140 F for 24 hours).

The length of the bars was carefully measured before and after this period of time. Although the unacceptable aggregate particles developed pronounced reaction shells which could be accentuated by acid etching of cut sections, the bars did not expand appreciably—the average expansion being less than 0.02 percent. Because this same expansion was experienced by the bars made with acceptable aggregate; that is, pure carbonate rocks (Tables 2 and 3) which did not develop reaction shells, it cannot be attributed to shell growth. Several photomicrographs of the reaction shells which develop are included in a previous publication (5).

There is no exact definition of "excessive expansion." It is generally considered that in an environment of 100 F over water, 0.10 percent expansion in six months of time is deleterious (10, p. 21).

To determine how the compressive strength of these concrete bars was affected by residence in environment C, the following tests were run.

Six bars were selected, four which developed reaction shells in environment C and

The method employed is described by Bisque and Lemish (5, p. 50).

Concrete bars were prepared according to the following formula: 750 gm Penn Dixie Type I cement (total alkali content reported as Na₂O is 0.51 percent according to ASTM C-114-58T); 2063 gm graded Ottawa sand (according to ASTM C-109); 100 ± 50 cc water. Cured 28 days in moist room.

two which did not. A companion bar (that is, made with the same aggregate at the same time) was selected for each of these from environment A. The bars were cut and capped according to ASTM methods (ASTM Designation C192-57) and the compressive strength measurements were made in accordance with an ASTM procedure (ASTM Designation C116-49). The results of these tests are given in Table 4.

For the concrete bars tested, the increase in compressive strength which resulted from residence in environment C was considerably less when shell growth occurred. These bars did not expand excessively (Table 3) and visual inspection of the broken fragments proved the presence of reaction shells.

To summarize, the experimental results given in Tables 1, 2, 3, and 4, demonstrate that the bars made with unacceptable aggregates supported chemical changes which resulted in:

1. An increase in silicon content of the aggregate with no accompanying increase in soda or potash content.
2. No expansion in excess of that experienced by companion bars made with acceptable aggregate when subjected to environment C.

TABLE 1
CHEMICAL ANALYSES OF AGGREGATE CHIPS BEFORE AND AFTER EQUILIBRATION WITH CONCRETE

Code ¹	Before			Na ₂ O (ppm)	K ₂ O ³ (ppm)	After			Na ₂ O (ppm)	K ₂ O ³ (ppm)
	% SiO ₂	% CaCO ₃ ²	% MgCO ₃ ²			% SiO ₂	% CaCO ₃ ²	% MgCO ₃ ²		
(a) Acceptable Aggregate										
OG-22	0.10	97.5	2.3	30	<10	0.11	97.5	2.3	30	<10
OG-24	0.90	96.5	2.1	20	<10	0.90	96.4	2.0	25	<10
(b) Unacceptable Aggregate										
OG- 1	7.25	74.7	12.9	15	<10	13.20	73.1	12.0	15	<10
OG- 2	16.25	64.0	15.3	25	<10	19.00	62.1	15.1	20	<10
OG- 4	15.20	59.2	21.2	20	<10	19.10	57.6	20.1	15	<10
OG- 5	16.10	57.4	18.1	10	<10	20.25	56.1	17.8	10	<10
OG- 7	11.30	-	-	10	<10	12.85	-	-	10	<10
BTN-14	14.30	-	-	30	<10	16.10	-	-	20	<10
BTN-15	10.75	-	-	10	<10	14.50	-	-	5	<10

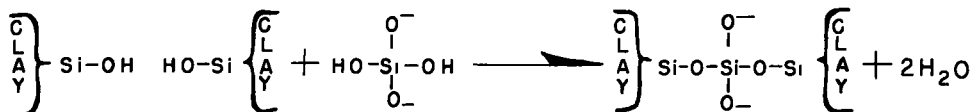
¹Code: OG - Glory quarry; BTN - Burton Avenue quarry.

²CaCO₃ and MgCO₃ were calculated from Ca and Mg determinations. Unacceptable aggregates are characterized by high insoluble residue content. The analyses do not include such constituents as Al₂O₃, iron oxides, SO₄.

³Less than 10 ppm in all cases.

3. A definite decrease in the amount of compressive strength gained during hydration in environment C.

None of the foregoing observations are in discord with the previously postulated mechanism for shell growth. A detailed discussion of this theory is included in another manuscript (4). The author visualizes the "tying together", or polymerization, of clay particles via a mechanism which might be represented as follows:



The terminology "clay particles" is meant to include both particles of well-ordered allitic clays and poorly or entirely disordered "groupings" of silica and alumina tetrahedra. The nature of such material is aptly described by Mason (9) who says "...as grain size diminishes so does perfection of crystallinity, and probably no sharp break exists between imperfectly crystallized clay minerals and amorphous material which may perhaps be looked upon as aluminosilicate gel."

By joining disseminated clay particles in a three-dimensional network, this reaction would account for the following observations:

1. It would result in an increase in silicon content of the aggregate particles with no increase in soda or potash content.
2. It would explain the appearance of the siliceous, skeletal structure which remains when the carbonate minerals are leached from the shell zone, Bisque and Lemish (5, Figs. 20 and 21).

TABLE 2
LENGTH CHANGES OF CONCRETE BARS WHICH WERE KEPT DRY AT
ROOM TEMPERATURE
(ENVIRONMENT A)

Bar Number	Measurement (inches from reference)	Change in Length (inches)	% Change (shrinkage)
(a) Acceptable Aggregate			
13	-0.0028 -0.0006	0.0022	+0.01 ¹
14	-0.0130 -0.0157	0.0027	-0.02
16	-0.0413 -0.0437	0.0024	-0.02
17	-0.0064 -0.0072	0.0008	-0.01
18	-0.0070 -0.0108	0.0038	-0.03
(b) Unacceptable Aggregate			
4	-0.0265 -0.0324	0.0059	-0.04
6	+0.0047 +0.0006	0.0041	-0.03
7	-0.0079 -0.0112	0.0033	-0.02
23	-0.0289 -0.0324	0.0035	-0.03
24	-0.0235 -0.0263	0.0028	-0.02
28	-0.0329 -0.0357	0.0028	-0.02
33	-0.0161 -0.0228	0.0067	-0.04
36	-0.0191 -0.0139	0.0052	-0.04
37	-0.0053 -0.0003	0.0050	+0.04 ¹

¹Slight expansion.

3. It would account for the definite decrease in effective porosity which accompanies shell growth, Bisque and Lemish (3, p. 39).

4. This type of reaction would not be expected to produce expansion of the aggregate particles because no siliceous gels are formed.

5. Because a source of silicon is required, it offers a very feasible explanation for the weakening effect observed. A critical amount of silicon may be removed from the cement paste.

6. Non-argillaceous aggregates do not develop these reaction shells.

Excellent support of this theory is found in a recent publication by Hiltrop and Lemish (7). The authors reasoned that because certain carbonate rocks readily "absorb" mobile silicon from either aqueous solution or from moist cement paste (3, 5), they may react in the same manner if placed in an atmosphere of vaporous silicic acid.

TABLE 3
LENGTH CHANGES OF CONCRETE BARS SUBJECTED TO WETTING
AND DRYING CYCLES
(ENVIRONMENT C)

Bar number	Measurement (inches from reference)	Change in Length (inches)	% Change (expansion)
(a) Acceptable Aggregate			
11	-0.0055 -0.0033	0.0022	+0.01
12	+0.0144 +0.0169	0.0025	+0.01
15	-0.0355 -0.0337	0.0018	+0.01
19	-0.0080 -0.0051	0.0029	+0.02
20	+0.0264 +0.0291	0.0027	+0.02
(b) Unacceptable Aggregate			
1	-0.0094 -0.0064	0.0035	+0.02
5	+0.0089 +0.0103	0.0015	+0.01
10	-0.0156 -0.0143	0.0013	-0.01 ¹
21	-0.0002 +0.0023	0.0025	+0.02
25	-0.0190 -0.0167	0.0023	+0.02
30	-0.0290 -0.0262	0.0028	+0.02
31	-0.0078 -0.0077	0.0001	0.0
35	-0.0320 -0.0326	0.0006	-0.01 ¹
40	+0.0150 +0.0164	0.0014	+0.01

¹Slight shrinkage.

The vapor was generated by allowing silicon tetrachloride (SiCl_4 , B. P. 58 C) to volatilize and to be hydrolyzed by water vapor in the atmosphere to form $\text{Si}(\text{OH})_4$.

After subjecting argillaceous carbonate rocks to this vapor, the authors noted two distinct changes in the rock: (1) a definite gain in weight, and (2) a siliceous skeleton remained after careful acid leaching of the treated rock. Comparison of a photomicrograph of this skeleton (7, Fig. 3) with a photomicrograph of a skeleton formed in aqueous solution (7, Fig. 21) reveals a striking resemblance. The experiment with silicon tetrachloride furnishes conclusive proof of the fact that shell growth can occur without the introduction of any element other than silicon.

CONCLUDING REMARKS

This study demonstrates that the chemical reactivity of all of the mineral species in

TABLE 4

COMPRESSIVE STRENGTH OF CONCRETE MADE WITH ACCEPTABLE AND UNACCEPTABLE AGGREGATE

Set 1 After Residence in Environment A—4 months		Set 2 After Residence in Environment C—4 months		Effect of Environment C
(a) Acceptable Aggregate (non-argillaceous)				
-Burton Solon-		-Burton Solon-		
Bar No. 17	4400 psi	Bar No. 20	6200 psi	
	4100		6500	
	4400		6400	
14	3500	11	6300	
	3500		5700	
	4100		6300	
Average	4000 psi	Average	6200 psi	+2200 psi
(b) Unacceptable Aggregate (argillaceous)				
-Burton Rapid-		-Burton Rapid-		
Bar No. 9 ¹	4200 psi	Bar No. 1	4300 psi	
	3800		3600	
	4100		4000	
7	4400	5	4400	
	4100		4600	
	3900		4200	
Average	4100 psi	Average	4200 psi	+ 100 psi
-Glory Rapid-		-Glory Rapid-		
Bar No. 27 ¹	4600 psi	Bar No. 30	5400 psi	
	4400		4900	
	5000		4800	
33	5100	21	5400	
	5000		4800	
	5100		5200	
Average	4900 psi	Average	5100 psi	+ 200 psi

Length changes for Bars No. 9 and 27 are not included in Table 3. Their expansion did not exceed 0.02 percent.

a rock must be considered in evaluating it as an aggregate. In this case a minor fraction of an otherwise suitable aggregate is responsible for causing it to react with a constituent of the cement paste. The environment which a rock experiences in portland cement paste is quite different from the types of environment generally considered when the "stability" of a rock is discussed. In concrete the aggregate is seeking equilibrium with a man-made "rock" which is unique in that it: (a) is relatively homogeneous as regards porosity and chemical composition; (b) supports a high pH; (c) is composed essentially of products of rapid hydration processes; and (d) is found in a wide variety of climatic and geologic settings.

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