

Chemical Characteristics of Some Carbonate Aggregate as Related to Durability of Concrete

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This report includes a summary of the results of the chemical study of carbonate rocks from several quarries in northeast Iowa which produced carbonate aggregate for highway pavement concrete.

Rock from one of the quarries has proven to be definitely unsatisfactory for use as aggregate and is being used as a comparative standard. Comparison is based on the three following phases of investigation:

1. Analysis for major constituents (chemical description of rock types).
2. Determination of the type and quantity of potentially reactive deleterious constituents contained in the aggregates.
3. Chemical analysis and study of aggregate taken from samples of affected concrete.

An investigation of the equilibria established between certain carbonate rocks and silica solutions at pH 12 is being carried out to determine what reactions take place.

● THE RESEARCH described in this report was carried on as part of a broader project sponsored by the Iowa State Highway Commission, the goal of which is the determination of causes of premature deterioration in pavement concrete made with carbonate aggregate and the development of standard laboratory procedures to aid in recognizing aggregates with potentially poor service records.

Standard tests for predicting durability of aggregate have been shown to be inadequate (25, 14), and test results on materials without demonstrated service records are in no way conclusive or definitive. There is a definite need for research to determine the properties of aggregate which influence its performance in concrete and for the development of standard procedures for determining the properties which are important in this respect.

This particular investigation is based on the assumption that aggregate may be involved in deleterious chemical activity which accompanies normal aging and produces stresses in concrete. The influence of the aggregate material may be manifested in two distinct ways: (1) it may contain "active" substances which are available for subsequent slow reaction with the cement paste; (2) the aggregate particles may function as mere physical "centers" of reaction, leading to localization of activity and resultant weak spots. Physical characteristics of the material such as porosity and permeability are no doubt of prime importance in the latter case.

A considerable amount of literature concerning the possible types of chemical activity that might be initiated by constituents present in concrete aggregate has been published in the journals and in laboratory reports of highway commissions. Of those examined, only a relatively few deal with carbonate aggregate and none has been found which is concerned specifically with the quantity of chemical substances which is contained in the aggregate and actually "available" for reaction in concrete. Certain deleterious chemical substances are recognized in aggregates of other rock types and their role in promoting deterioration has been studied rather carefully. Since the presence of these same substances in limestone aggregate would lead to similar types of stress, their effects will be briefly reviewed.

Most published discussions of deleterious chemical substances in concrete emphasize the effects of excess sulfate ion and of free silica. Although gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

is added to portland cement as a retarding agent and in this capacity is both desirable and necessary, excess sulfate introduced with aggregate or by some outside source is definitely deleterious (13, 15, 19). Free or "reactive" silica is another undesirable constituent which may be introduced with the aggregate. Silica in certain forms is known to react with caustic from the cement and produce siliceous gels or sols which are believed to be a major cause of stress. This type of activity is commonly referred to in the literature as the "alkali-aggregate reaction" and extensive studies have been carried out to determine the exact nature of the reaction itself and the mechanism of the stress caused by the reaction products (3, 5, 7, 8, 17, 23, 26). Although the various papers pertaining to the alkali-aggregate reaction represent an impressive body of research, the exact mechanisms of the process have by no means been fully worked out. It is generally agreed, however, that certain forms of reactive silica definitely contribute to chemical activity which results in physical stress.

Another undesirable substance which may be introduced with carbonate aggregate and which may be involved in chemical activity is clay. Although the clay minerals are not chemically active constituents in the same sense as are the sulfate ion and silica, it has been postulated that clay particles may promote deterioration either by functioning as centers of activity or by swelling and movement of the clay particles themselves. It is reasonable to assume that a clay particle, which retains water and has available certain exchangeable cations, may contribute to or enhance chemical activity in concrete. Clay is not an uncommon constituent of limestone. Grim's analysis of 35 Paleozoic limestones from Illinois showed illite in all of them (6).

There are a number of other chemical substances which are not commonly present in aggregate in appreciable quantities but have been shown to be deleterious to concrete when introduced from some outside source (22). Among these are sodium and calcium chloride and numerous salts present in sea water.

INVESTIGATION

The data used as the basis for the discussion in the first two divisions of this section (that is, Phase 1 and Phase 2) are taken mainly from an unpublished theses (2) and have been supplemented by analyses run since the thesis was written. Carbonate rocks of Devonian age were sampled from five quarries on a bed by bed basis (12). The values reported in Tables 1 and 2 are averages arrived at by analysis of composite samples which were prepared by mixing powdered portions of each sample in proportion to their relative thickness in the formation member. The figures were since checked against values arrived at by averaging the results of analyses run on each lithologic unit (bed) of the same members. The differences in resultant values were not significant.

The Rapid member of Glory Quarry, now abandoned, has a notorious service

TABLE 1
ANALYSES FOR MAJOR CONSTITUENTS (PHASE 1)

Members and Approximate Thickness in Feet	Calcium (as CaCO ₃) %	Magnesium (as MgCO ₃) %	Insoluble Residue %	Fe %
Glory Quarry				
Lower Rapid (19)	63.5	20.5	13.75	0.25
Upper Rapid (14)	54.0	20.0	16.16	0.28
Coralville (7)	90.5	5.5	2.86	0.08
Newton Quarry				
Total Rapid (28)	65.0	29.0	4.26	0.16
Coralville (20)	73.0	21.5	4.05	0.11
Burton Ave. Quarry				
Solon (31)	88.8	5.0	5.04	0.15
Lower Rapid (14)	58.5	22.5	16.45	0.22
Upper Rapid (22)	46.0	29.5	21.63	0.25
Coralville (12)	68.5	26.0	4.66	0.34
River Products Quarry				
Solon (22)	71.0	14.5	11.95	0.30
Total Rapid (13)	75.0	12.5	8.90	0.37
Coralville (42)	92.0	3.0	1.96	0.13
Pints Quarry				
Total Rapid (23)	56.0	27.5	5.45	0.13
Coralville (24)	75.0	23.0	1.44	0.19
Coralville ^a (24)	71.0	26.5	1.60	0.17

^a Weathered

TABLE 2
CONSTITUENTS EXTRACTED (PHASE 2)

Members and Approximate Thickness in Feet	Base Reacted %	SiO ₂ Extracted (mg/100 gms)	Gypsum Extracted %
Glory Quarry			
Lower Rapid (19)	50	38.6	0.10
Upper Rapid (14)	72	49.0	0.25
Coralville (7)	22	9.7	0.02
Newton Quarry			
Total Rapid (28)	40	20.1	0.05
Coralville (20)	33	20.4	0.04
Burton Ave. Quarry			
Solon (31)	28	14.7	0.02
Lower Rapid (14)	64	52.0	0.14
Upper Rapid (22)	61	41.2	0.14
Coralville (12)	98	36.8	0.14
River Products Quarry			
Solon (22)	98	45.0	N. D. ^a
Total Rapid (13)	98	39.2	0.16
Coralville (42)	22	16.0	0.05
Pints Quarry			
Total Rapid (23)	32	28.9	Trace
Coralville (24)	28	9.8	Trace
Coralville ^b (24)	96	18.3	N. D.

^a Non detected.

^b Weathered.

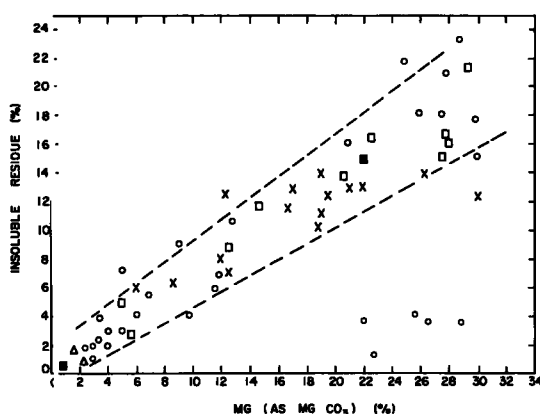


Figure 1. Relationship of insoluble residue and magnesium content. Data from Bisue (2) (composite samples of formation members) and results of analyses of lithologic units from four different quarries (Phase 1).

residue. These results are used as a "chemical description" of each lithologic unit and their values used to compare lithologic units as to "purity" based on implied carbonate content (that is, carbonate itself is not determined directly).

Powdered samples are dissolved by heating in 3N HCl at 80 C for 30 minutes. The remaining insoluble portion is separated by filtration with suction on a medium sintered glass filtering crucible. The dry weight of this portion (dominantly SiO_2 and in some cases small amounts of pyrite and clay) is the reported insoluble residue. The filtrate is transferred, diluted to volume in a volumetric flask and aliquots taken for determination of calcium and magnesium via a volumetric method utilizing the complexometric properties of Versene (ethylene-diamine-tetraacetic acid). The principles of this procedure are described by Cheng et al. (4) in a brief publication.

In examining the data of analyses of samples from six quarries it was observed that a definite correlation exists between the amount of insoluble residue and the magnesium content. This relationship is shown in Figure 1. The results of analyses of limestones from the five main quarries being considered are averaged in Table 1, and will be referred to in subsequent passages.

In instances where it was desirable to determine the iron and aluminum content of certain limestones (see Phase 2, Clay), Versene was again employed. The procedure involves first the determination of the sum of aluminum and iron in one aliquot and then the determination of iron alone in another. Aluminum is calculated by difference. The total is determined by causing both aluminum and iron to react with a known amount of Versene by boiling at low pH and then determining the amount of excess reagent by back titrating with standard zinc solution. Dithizone (diphenylthiocarbazone) is used as an indicator and the zinc-Versene back-titration must be buffered at pH 4.4 in a 1-1 methanol-water mixture. If present in appreciable amounts, iron may then be determined in another aliquot by titration with Versene solution to a salicylic acid end point at pH 3.5 as described by Cheng et al. (4). Small amounts of iron are best determined colorimetrically.

The method is applicable in cases where the aluminum content is desired to within 10 percent relative error. Its relative simplicity as compared with tedious gravimetric procedures which are themselves susceptible to numerous sources of error, makes the procedure desirable for routine analyses of this sort where relative values (that is, comparison of rock A to rock B) are more important than highly accurate, absolute determinations. Publication of the details of this procedure utilizing Versene for the determination of Ca, Mg, Fe and Al in limestones is forthcoming from this laboratory.

record as concrete aggregate and is being studied as a comparative standard.

The investigation may be divided into three phases, each of which will be treated separately in the following order.

Phase 1. Routine analysis of each lithologic unit for its major constituents.

Phase 2. Determination of the type and quantity of potentially "available" deleterious chemical constituents (including clay) in the samples.

Phase 3. Investigation of "affected" concrete samples from highways which have been constructed with poor aggregate from known sources. Limestones from these same sources are also treated in Phases 1 and 2 of the investigation.

Phase 1

The "major constituents" determined were calcium magnesium and insoluble

Phase 2

Since the pH of water in equilibrium with portland cement concrete is in the range of 11-12, only those constituents which might leach or "extract" into a basic solution were considered available for reaction. Powdered rock samples (50 gm) were agitated with 450 ml of a dilute solution (0.008 M, pH 11.4) of sodium hydroxide for 12 hours in polyethylene bottles. The mixture was then allowed to settle and the liquid separated by filtration. An aliquot of the filtrate was titrated to determine the decrease in basicity and the remaining portion analyzed for leached substances. Ions detected in appreciable amounts were Ca^{++} , SO_4^{--} and SiO_4^{--} . Mg^{++} and traces of Cl^- were also common.

Sulfate. Although gypsum or other sulfate minerals were not detected in thin-section analysis of the rocks subjected to this extraction, the quantity of sulfate found in the filtrates is worth noting (Table 2). This sulfate was very readily dissolved from the powdered rock and easily detectable amounts were leached by placing the powdered sample in a filter funnel and merely allowing several hundred milliliters of distilled water to pass on through. To then determine whether the sulfate is readily leached from aggregate-sized particles, the extraction was modified. Approximately 50 pieces of these particles were placed in a separatory funnel and saturated with the same weakly basic solution. By allowing the solution to escape slowly from below and replenishing the supply from another separatory funnel at a comparable rate, it was possible, in two days time, to extract from 40 to 60 percent of the total amount of sulfate which was extracted from the same sample in powdered form. The results indicate that the sulfate present is not "locked" in the aggregate and may be available for reaction in concrete. The source of sulfate is assumed to be disseminated gypsum (10).

Sulfate was determined by the standard method of precipitating with barium ion in acid solution.

Silica. Larger samples of powdered rock were extracted in the manner described and the quantity of leached silica in the filtrate determined by the standard double dehydration procedure after removal of the dissolved sulfate by slow precipitation with barium. The amount of silica found correlated with the decrease in basicity is shown in Figure 2. When blanks were run it was found that a small amount of base "reacted" with reagent grade calcium carbonate or with powdered calcite rhombs. This amounted to 0.44 milliequivalents of the available 3.60 milliequivalents of base (that is, 450 ml of 0.008N NaOH) and is attributed to the complex equilibria involved in the hydrolysis of the carbonate ion.

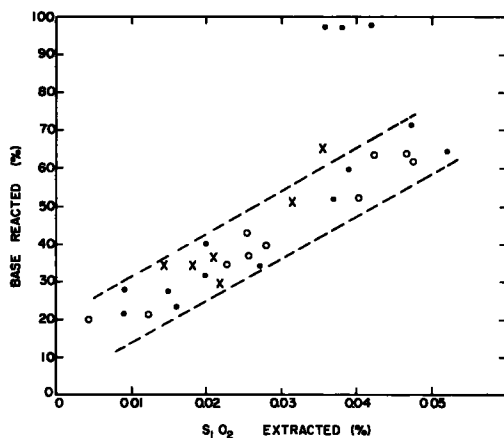


Figure 2. Relationship of the quantity of silica extracted to the amount of base reacted (Phase 2).

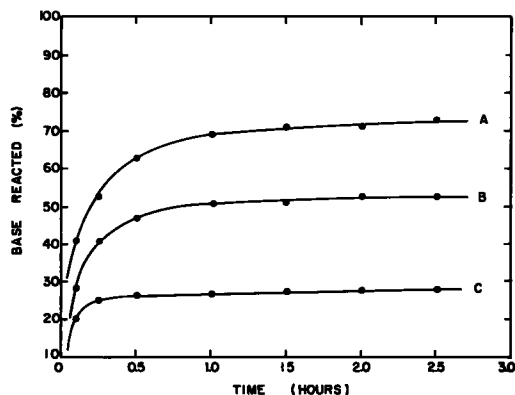


Figure 3. Rate of base reactivity for three samples from the Glory Quarry. Amount of base reacted after 12 hours; A, 76 percent; B, 54 percent; C, 29 percent.

Three interesting facts concerning this extraction procedure were noted. (1) The relatively rapid rate at which the base was consumed by those rocks which displayed base reactivity; 80 to 90 percent of the total amount which finally reacted had reacted in 30 minutes, Figure 3. (2) The

amount of silica extracted from samples of different lithologic units showed no relation to the abundance of chert nodules as observed in the respective units. (3) Finely powdered (passing No. 100 sieve) chert nodules taken from the limestone beds consumed considerably less base (1.0 meq of the available 3.6 Meq's) and yielded far less soluble silica than many of the limestone samples did.

These observations would support the postulation that the "available" or "reactive" silica extracted from the limestones is in some physical form distinct from that which it exhibits when aggregated to form chert. The concept of a reactive state of silica characterized by disrupted silicon to oxygen bonds and a general disorderly atomic arrangement which renders it more soluble is well recognized (21). Silica which is free to migrate or diffuse through carbonate rock must necessarily exist in some such physical state. The equilibria between soluble, amorphous and crystalline silica are little understood and the formation of authigenic silicates further complicates natural systems. For a recent publication concerning the dissolution and precipitation of silica at low temperatures the reader is referred to (9).

In connection with the discussion of reactive silica, another interesting fact was observed. This was a correlation between the amount of iron dissolved in Phase 1 and the amount of silica leached from the same rock in Phase 2 (Fig. 4). Since pyrite is insoluble in hydrochloric acid, the iron which was brought into solution via the procedure described in Phase 1 was assumed to originate from iron oxides present in the limestone. The correlation is at first puzzling but on further consideration is found to be compatible with the concepts reviewed in the following paragraph.

Conditions which tend to render silica mobile are conditions which would stabilize or "fix" dissolved iron as the oxide. Conversely, conditions which would mobilize iron would permit minimum activity of silica. These facts are borne out by numerous geologic processes such as laterization (18), residual concentration of iron (1), and the chemical nature of the elements themselves. Hence in the case of a rock whose recent history involved conditions which resulted in silica activity, and an increased proportion of reactive silica, stabilization and retention of any iron entering the environment in solution would occur. The observed correlation is at least harmonious with basic principles that are manifested in geologic processes.

Clay. A considerable amount of effort was expended in developing a suitable method for the separation and concentration of the clay fraction with a minimum amount of "damage" to the clay structure. A relatively simple and very satisfactory separation was effected as follows.

Fifty grams of finely powdered rock (passing No. 100 sieve), 50 ml of dispersing agent,¹ and several hundred ml of distilled water were agitated for five minutes in a mechanical laboratory stirrer. This suspension was then transferred into a 1,000 ml graduated cylinder and more water added. The system was again thoroughly agitated with a mixing plunger and allowed to stand for 7 hours at room temperature. A 50 ml aliquot was then taken at a depth of about 5 cm and placed in a centrifuge bottle. The aliquot was centrifuged for 15 minutes at 2,500 rpm and the supernatant decanted, leaving a heavy slurry clinging to the bottom of the bottle. Ten ml of distilled water were added and the slurry stirred into suspension. Exactly 4 ml of the resulting suspension were drained onto a 25 by 46 mm glass slide which was previously placed in an oven pre-heated to 60 C. After several hours the dry slide is found to be covered with a uniform coating suitable for X-ray diffractometer investigation.

The only clay type found in appreciable amounts was illite. Sixty percent of the rock from the Rapid member at the Glory Quarry which averaged 15 percent insoluble residue, contained appreciable amounts of the clay mineral. No trace of illite was found in the entire section of Mississippian rock exposed at the Alden Quarry which averages less than 1 percent insoluble residue. Alden Quarry aggregate has an exceptionally good service record (20). The Rapid member at Pints Quarry (average insoluble residue, 5 percent) contained appreciable illite whereas the overlying Coralville member (average insoluble residue, 1.5 percent) showed no trace of the mineral.

¹ Prepared by dissolving 40 gm of sodium meta silicate, $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$, and 7 gm sodium carbonate, Na_2CO_3 , in water and diluting the solution to one liter.

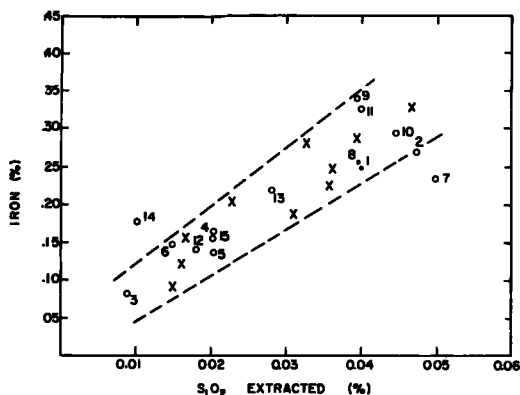


Figure 4. Relationship of the percent of soluble iron (Phase 1) to the quantity of silica extracted (Phase 2).

The Solon member at the Burton Ave. Quarry (average insoluble residue, 5 percent) showed only a trace of illite whereas the overlying Rapid member (average insoluble residue, 18 percent) yielded slides which gave excellent, intense diffraction patterns of the mineral. The Coralville member in this quarry (average insoluble residue, 4.5 percent) displayed less intense spectra via the same procedure. The diffraction patterns of the samples from the Rapid member in this quarry were so intense that the rate meter scale factor of the X-ray recorder (North American Phillips Co.) which was normally set at 4, had to be switched to 8 in order to record the intensity of the 10 angstrom reflection.

The X-ray diffraction pattern of a typical sample is shown in Figure 5 along with the diffraction pattern of a "clay mineral standard" from Fithian, Illinois. A third

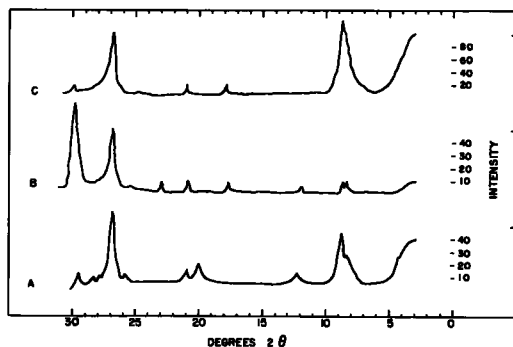


Figure 5. Relative intensity of major reflections of A, Fithian illite; B, Fithian illite-calcium carbonate mixture; and C, illite separated from a Burton Avenue Quarry sample (Phase 2).

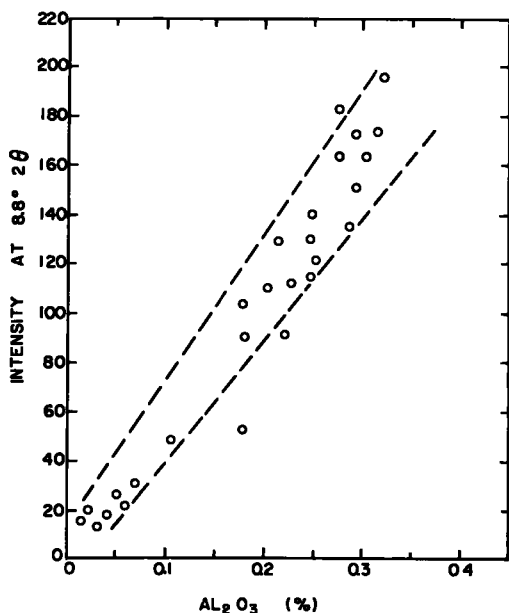


Figure 6. Intensity of 10 angstrom reflection from glass slides coated with illite separated from Burton Avenue samples (Phase 2) vs the quantity of aluminum found in the same rock (Phase 1).

diffraction pattern is included to show the effect of mixing the standard illite with calcium carbonate in a 1:1 ratio before depositing it on the glass slide in the manner previously described. The orientation of the clay particles has obviously been affected and the carbonate reflection at 29.45 deg 2θ (dA, 3.03; θ, 14.73 deg; hkl, 104) is very prominent. By comparing the intensity of this carbonate reflection in this diffraction pattern with the same reflection in the diffraction pattern of illite from a Burton Ave. sample it can be seen that an excellent separation has been effected. Glycolation caused no noticeable expansion of the illites separated from any of the samples being investigated.

To observe how the amount of dissolved aluminum (Phase 1) compares with the intensity of the illite diffraction pattern from the same rock (Phase 2), the samples from Burton Ave. Quarry were analyzed for aluminum via the method previously described, and these values plotted vs the recorded intensity of the clay pattern at 8.8 deg 2θ (dA, 9.9 deg; θ, 4.4 deg; hkl, 001). The resulting relationship shown in Figure 6 would imply

TABLE 3
ANALYSES OF AGGREGATE FROM SAMPLES OF AFFECTED CONCRETE
(PHASE 3)

Aggregate with No Visible Reaction Rims			Aggregate with Less Pronounced Reaction Rims			Aggregate with Pronounced Reaction Rims		
Insoluble Residue (%)	CaCO ₃ (%)	MgCO ₃ (%)	Insoluble Residue (%)	CaCO ₃ (%)	MgCO ₃ (%)	Insoluble Residue (%)	CaCO ₃ (%)	MgCO ₃ (%)
4.19	85.75	8.73	13.38	56.50	26.38	13.24	57.00	27.74
4.26	83.81	11.61	12.82	54.11	31.88	14.10	55.21	28.12
3.10	87.11	9.13	-	-	-	13.13	56.52	27.98

TABLE 4
ANALYSES OF REACTION RIM
MATERIAL FROM AFFECTED
CONCRETE (PHASE 3)

Insoluble Residue (%)	CaCO ₃ (%)	MgCO ₃ (%)
A. 19.80	56.12	23.70
B. 17.41	61.00	23.85

that the illite is the main source of dissolved aluminum and that the quantity of illite separated, as indicated by the intensity of its basal reflection, is an approximate indication of the amount present in the rock. This plotted relationship would cease, however, when the optimum thickness of the illite layer on the glass slide was reached.

Phase 3

Considerable time was spent in examining the petrographic and chemical characteristics of the aggregate in affected concrete. Bulk samples of concrete were taken from the sites of highway repair in north-east Iowa. The sampled chunks were reduced to gravel size and examined for evidence of secondary deposits.

A white substance found lining small vesicles in the cement paste was removed by prying with a needle point. A portion of the quantity separated was analyzed by wet methods and the remainder subjected to spectrographic analysis. It was found to be almost pure calcium carbonate, the major impurity being magnesium. The migration of calcium carbonate in concrete is not uncommon (11). No evidence of silica gels as described in the literature (3, 15) was found. A few secondary deposits, presumably calcium sulfo aluminate, were found to contain sulfur. No visible effect of clay was expected to be observed, of course, but aggregate particles which had the chemical characteristics of limestone which frequently contains appreciable clay (that is, high insoluble residue and high magnesium content) were usually concentrated in the most highly affected areas, as judged by the relative amounts of secondary deposits.

Many of these same aggregate particles displayed marked zones or rims along their periphery adjacent to the cement paste. These zones were accentuated by their color, which varied from that of the host rock. A description of thin-section examinations of these zones is included in the accompanying report (12). In contrast to the aggregate particles with marked rim zones were those which were completely unaltered at their borders and still others which displayed less salient rim zones. These three aggregate "types," based on visible appearance of rims, were sampled and analyzed. Each sample contained at least 50 gms of carbonate rock from the unaffected, central portions of the aggregate type designated. No portion of the rim zone was included and no more than one gram was taken from a given aggregate particle. The results of these analyses are shown in Table 3. The aggregate which develops rims is consistently higher in insoluble residue and magnesium content than that which does not.

The rim zones were then sampled by tedious chipping and filing. Any cement paste which adhered to the outer margin of the rims was carefully filed away. The inner margin, however, was less abrupt (the unaffected aggregate-rim boundary) and portions

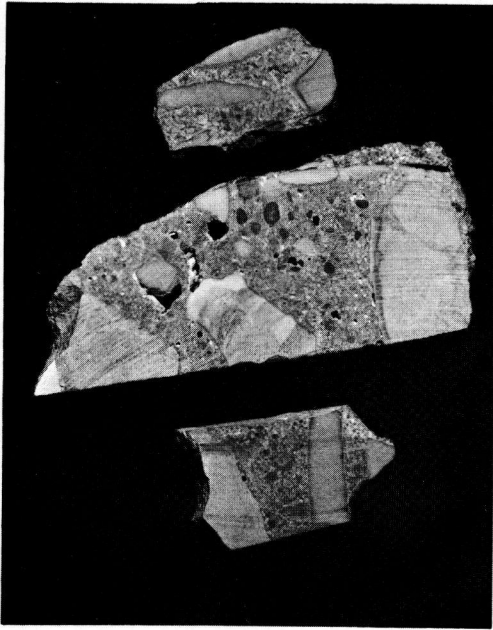


Figure 7. Section of a core taken from a distressed highway constructed with Glory aggregate. Note rims.

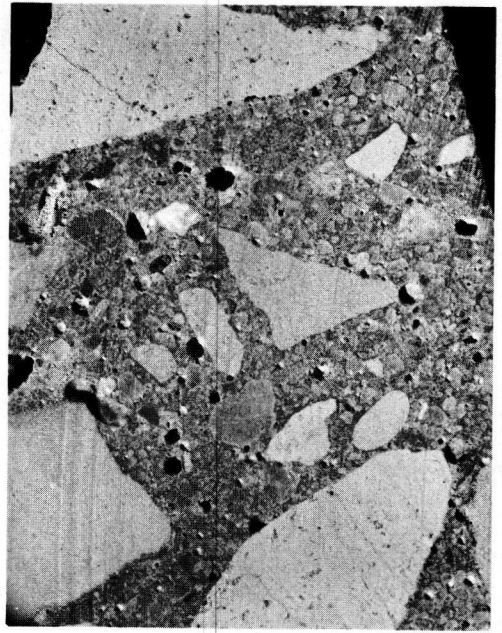


Figure 8. Section of a core taken from a sound highway. Compare with Figure 7.

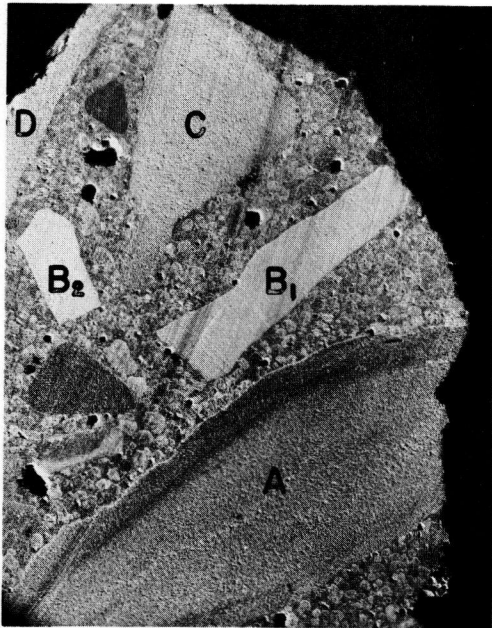


Figure 9. Surface of a piece of affected concrete. A, aggregate particle with rim. B₁ and B₂, lithographic limestone. C and D non-lithographic carbonate rocks with no rims.



Figure 10. Acid etching readily attacks the pure limestones (B₁ and B₂ in Figure 9). Note that the aggregate-cement paste boundary of these particles is sharp.



Figure 11. Further leaching has removed the lithographic particles. The boundary zone of particle A (Fig. 9) and the cement paste has already been attacked quite severely.

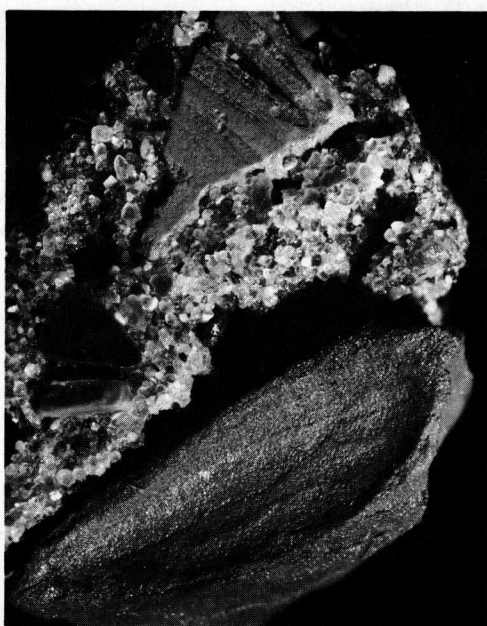


Figure 12. Advanced leaching has deeply entrenched the boundary zone of particle A and the cement paste while the rim stands in marked relief (see also Fig. 13).

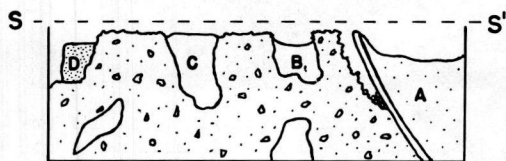
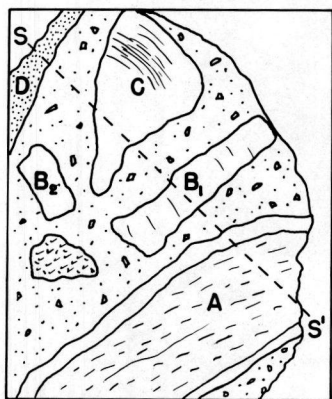


Figure 13. Sketch of cross-section through leached sample to demonstrate relative rates of solubility.

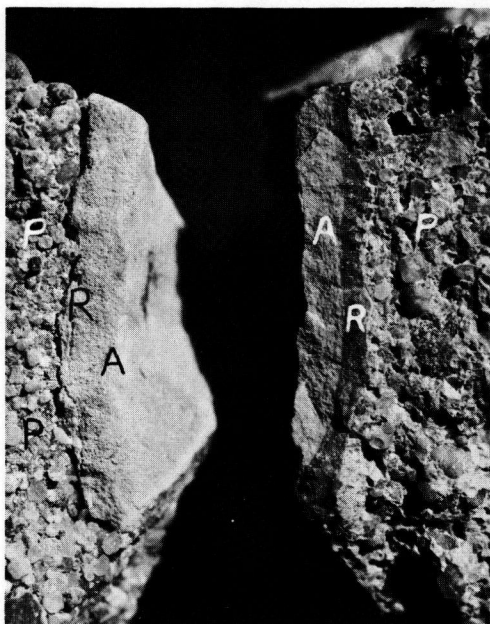


Figure 14. Two pieces of the same rimmed aggregate particle and adjacent cement paste. Before acid etching, right, and after slight etching, left. Note the readily attacked zone at the aggregate-paste boundary. A, unaffected aggregate; R, rim; P, cement paste.

of unaffected aggregate were not entirely removed in many instances. The analyses of two representative samples of rim material, 10 gms from at least 50 different pieces of aggregate A, and 5 gms from at least 30 different pieces of aggregate B, are included in Table 4. The rim zone shows a marked increase in insoluble residue and a decrease in magnesium content. The increase in insoluble residue was assumed to be due to an increase in SiO_2 content since the rim zones could be accentuated in relief by etching the affected aggregate with HCl . A piece of rim material placed in hydrochloric acid, along with a piece of the unaffected host rock, usually dissolved much more slowly; and if agitation was prevented, a "spongy" skeletal structure retained its identity. In many cases these rim particles were buoyed to the top of the solution by entrapped bubbles.

The observed decrease in magnesium content has not yet been thoroughly substantiated as being consistent.

The differential solution of rim zones and host rock is quite striking, and is illustrated in Figures 9 to 12 and an accompanying sketch, Figure 13. Figures 9 to 12 are a sequence of photographs taken at intervals during the progressive hydrochloric acid leaching of a piece of affected concrete taken from a distressed highway containing Glory aggregate. Rock A is an impure, argillaceous stone typical of the Rapid member of the Glory Quarry which usually develop rims in affected concrete. Rocks B_1 and B_2 are light-colored, ultra-fine grained lithographic limestones; that is, high CaCO_3 content, low MgCO_3 and insoluble residue content. Their lithographic character is evidenced by their very rapid solution in hydrochloric acid (see Figs. 10 and 11). Rocks C and D are not lithographic in character, nor do they have the "dirty," argillaceous appearance, or characteristic, of Rock A and other rocks (see Fig. 7) which develop rims. The cross-section in Figure 13 was sketched to show the approximate relationships of the rate of solution of the different zones in the sample, and to demonstrate the fact that the cement paste adjacent to the rimmed aggregate is more readily attacked by the hydrochloric acid than is the paste adjacent to the unrimmed particles.

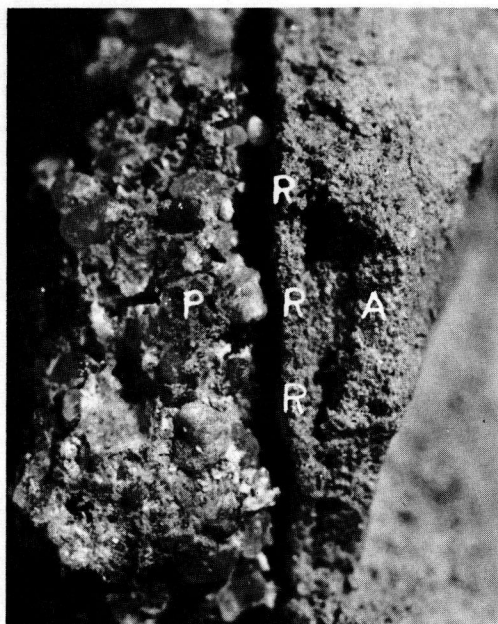


Figure 15. Close-up of a third piece of the same rimmed particle shown in Figure 14 after further acid leaching. A, unaffected aggregate; R, rim; P, cement paste. Note the marked differentiation of the rim zone.



Figure 16. Another example of rim differentiation after mild acid leaching. Note that in this case a more soluble zone occurs on the inner side of the rim. A, unaffected aggregate; R, rim; P, cement paste.

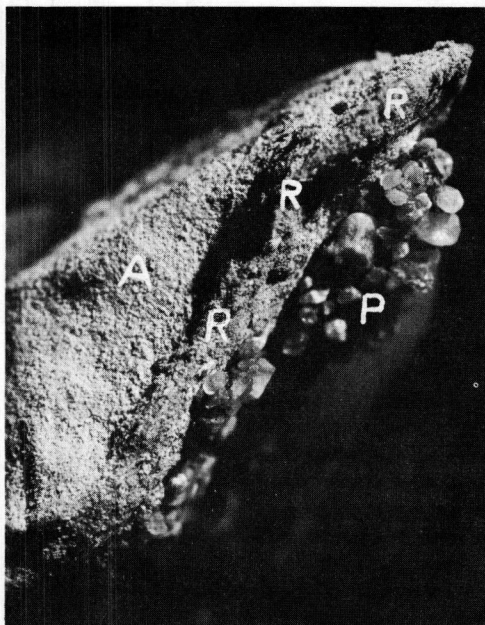


Figure 17. Rim zone accentuated by advanced leaching. A, unaffected aggregate; R, rim; P, cement paste.

In this instance a zone of increased solubility has formed on either side of the rim zone.

Advanced acid leaching of still another sample (Fig. 17) has left the rim zone standing high in relief, while the host aggregate and the cement paste have disintegrated at a much more rapid rate.

The pictures referred to in the preceding paragraphs show but a few examples of many such leachings which have been effected. The marked differences in the acid resistance of these zones leads the authors to the inescapable conclusion that chemical activity and accompanying transfer of material have occurred.

A concurrent study of the effective porosity and pore size distribution of potential aggregate rock is being conducted by Lemish et al. (12) of this laboratory. The device being used is a mercury capillary pressure apparatus manufactured by the Ruska Instrument Corporation, of Houston, Texas. The average effective porosity (that is, $\frac{\text{volume of mercury injected}}{\text{bulk volume}} \times 100$) of the aggregate from the Rapid member in the Glory Quarry was 6.2 percent, while the average effective porosity of the rim zone material taken from aggregate of this type in affected concrete was only 0.2 percent.

TABLE 5
ANALYSIS OF INSOLUBLE RESIDUES FOR SiO_2

Insoluble Residue of Aggregate (%)	Insoluble Residue of Rim Material (%)	SiO_2 Content of Insoluble Residue (Aggregate) (%)	SiO_2 Content of Insoluble Residue (Rims) (%)
12.61	16.23	87.0	86.3
11.24	15.12	90.6	89.8
13.88	17.64	89.5	89.2

This same general relationship was readily apparent in a majority of the samples of affected concrete which were leached. It can be seen that while the lithographic limestone particles dissolve quite readily, the paste adjacent to them is relatively unaffected by the same degree of acid treatment. Likewise, the cement paste adjacent to particles "c" and "d," which have no rims, is less affected than the paste adjacent to the rimmed aggregate A.

Figure 14, which pictures two portions of the same rimmed aggregate particle, one of which has been leached with dilute hydrochloric acid and the other unleached, clearly shows the marked increase in acid attack at the aggregate-paste boundary. Figure 15 shows the result of continued leaching of a third portion of the same aggregate particle and the adjacent cement paste. The resistance of the rim zone to leaching is very apparent, and the increased susceptibility to acid attack of the zone at the aggregate-paste boundary is quite distinct.

In Figure 16, the acid leaching of another rimmed aggregate particle again demonstrates that the rim zone is distinct.

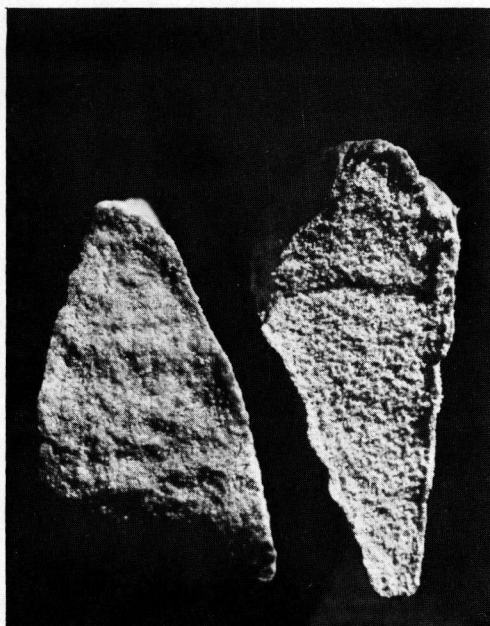


Figure 18. Two halves of a piece of Glory stone (Sample 4, Table 6) after 20 days in a 0.5 percent SiO_2 solution at pH 12. The half on the right has been acid leached. Length of particle, 1 cm.

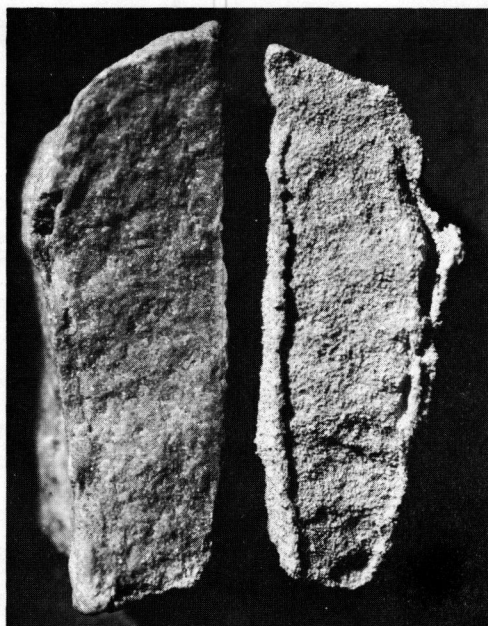


Figure 19. Two halves of a piece of Glory aggregate (Sample 3, Table 6) after 20 days in a 0.5 percent SiO_2 solution at pH 12. The half on the right has been acid leached. Length of particle, 1.5 cm.

The rim material used in this determination was filed free of all host aggregate and cement paste. It was felt that filing the rim particles might affect the results of effective porosity measurements. A sample of limestone, reduced to comparable-sized chips, and filed to smoothness, was subjected to mercury injection and the results compared with those determined on the natural rock. It was found that the change in effective porosity due to filing was negligible.

When the first draft of this report was submitted to the Committee on Durability of Concrete—Chemical Aspects, at the Annual Meeting of the Highway Research Board (1958), the results of analyses shown in Table 4 were questioned, for two reasons: (a) representability of sampling; and (b) analyses of the insoluble residues for SiO_2 were not reported.

Since that time, analyses of additional samples have been performed and the increase in insoluble residue content was found to have been accompanied by an increase in SiO_2 content (Table 5). The SiO_2 was determined by fusing the insoluble residues with sodium carbonate and utilizing the standard hydrochloric acid double dehydration procedure. Determination of calcium and magnesium in the rim zone was impossible in this case because the rim zone was separated from the affected cement paste by leaching with dilute hydrochloric acid. This, of course, resulted in the loss of carbonates from the rim zone. The siliceous, skeletal structure of the zone remained intact, however, and permitted a physical separation. It is true that some silica may have been leached from the rim zone by the dilute acid.

To further investigate the type of activity indicated by the foregoing observations, an entirely different approach was taken. This approach was based on the assumption that if certain carbonate rocks have a tendency to "react" with some form of soluble silica in a high pH environment, this tendency might be demonstrated in the laboratory.

TABLE 6
ANALYSES OF GLORY STONES USED IN RIM EXPERIMENTS

Sample No.	CaCO ₃ (%)	MgCO ₃ (%)	Insoluble Residue (%)	FeO (%)	Al ₂ O ₃ (%)
3	66.8	19.6	10.6	0.28	0.48
4	62.3	21.7	13.4	0.46	0.38
5	63.3	19.8	14.2	0.33	0.44
6	61.7	22.6	13.1	0.34	0.17

It was observed that solutions of silica² in reaching equilibrium with carbonate rocks of the Rapid-type lithology became yellow-colored and the color increased with time. Duplicate samples of the same rock in sodium hydroxide solution at pH 12 gave no discoloration whatsoever in the same period of time. After two weeks several pieces of rock were removed from the silica solution, broken and examined under a petrographic microscope. Faint lines were observed along the periphery of the broken particles. These lines appeared slightly darker than the host rock, and were not present as a "skin" on the aggregate particles, but actually a few millimeters inside the surface. Samples of the same rock which had been in a sodium hydroxide solution at the same pH, for the same length of time, had not developed these visible lines.

As the rock particles began to dry out, the lines became more difficult to see. Etching with 3N hydrochloric acid resulted in differential solution which dramatically accentuated the narrow zones. See Figures 18 and 19, each of which show two halves of a broken particle. In both figures, the particle half on the right has been acid leached to accentuate the line which is not here visible in the unleached half. Figure 20 is a close-up of the leached surface in Figure 18.

The "ridge" which stands in relief after etching is generally wider than the faint line observed before etching. A thin layer of host rock is etched away from the outer boundary of the "ridge," making it appear as though the more insoluble zone extends to the very outer edge of the particle. When slow etching is observed under the microscope, however, it can be seen that a very thin "outer shell" has dissolved away. It has been suggested that this zone corresponds to the highly acid-soluble zone at the aggregate-cement paste boundary in affected concrete samples (see Fig. 13). It should be pointed out, however, that during acid leaching of affected concrete samples, this thin zone dissolves much more readily than the corresponding host aggregate particle.

Samples of several lithologic units from the Rapid member in the Glory Quarry (Table 6) were placed in both sodium silicate and sodium hydroxide solutions for a week. In each case, the solution containing silica became yellowed and the hydroxide solution remained perfectly clear. Since both solutions were at pH 12 throughout the experiment, and both contained sodium ion, it might be concluded that the silica in solution is responsible for the observed "activity" and the development of "rims" in the system.

The results obtained in two additional attempts to experimentally substantiate this postulation are worthy of mention.

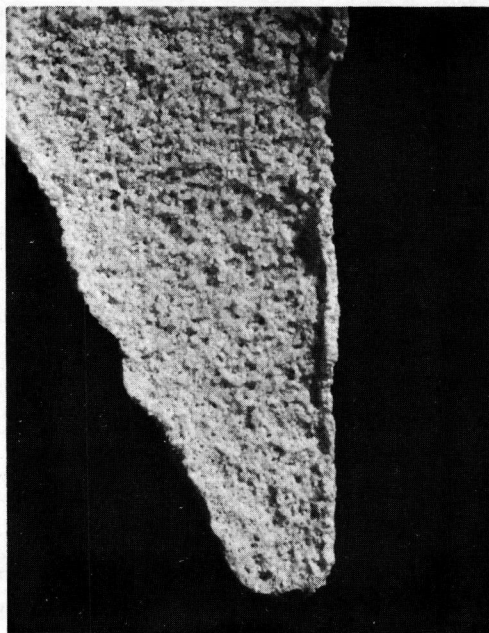


Figure 20. Close-up of leached particle shown in Figure 18.

²The silica solutions used in these investigations were prepared by dissolving 23.70 gms of sodium meta silicate, Na₂SiO₃ · 9H₂O, in one liter of distilled water. Such a solution contains 0.50 percent SiO₂ (by weight), or 0.50 gms SiO₂ in 100 ml, and is buffered at pH 12.

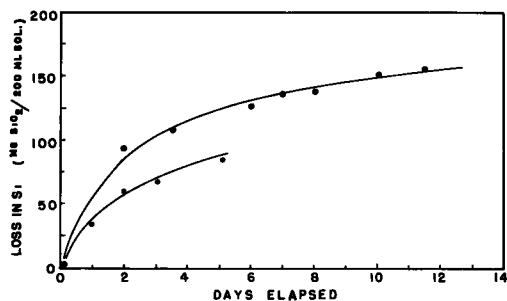


Figure 21. Decrease in SiO_2 content of a silica solution (pH 12) in equilibrium with certain carbonate rocks. Glory No. 6, 7 points determined and Glory No. 5, 4 points determined. See Table 6.

equilibrium with the impure carbonate rock was definitely depleted, quite rapidly at first and then gradually slower (Fig. 21). Analyses of the solutions in the three blanks showed no appreciable decrease in silica nor did any of the solutions become discolored. The procedure was repeated using sample 5 (Fig. 21).

2. The development of a yellow color was considered quite interesting since the solubility of iron would be negligible at pH 12. It was observed that during the evaporation of acidified aliquots taken from the carbonate rock-silica solution systems, a brown flocculent precipitate formed before the silica began to separate. Some of the brown precipitate was collected on a filter paper and subjected to spectrographic analysis. It contained iron and aluminum with a trace of calcium, magnesium, and manganese. The introduction of iron and aluminum into the solution while silica is being depleted might lead one to suspect that clay is involved. The rock samples involved did contain illite.

Attempts to develop the color of the 1, 10-phenanthroline complex of ferrous iron (after reduction) in the silica solutions were unsuccessful, probably due to the formation of a silicate-iron complex in solution. To establish whether the amount of iron "entering" the silica solution is a function of the silica concentration, a series of samples was prepared as follows.

Exactly 30 gms of carbonate rock (Glory No. 3, passing No. 10 sieve retained on a No. 32 sieve) were placed in each of six volumetric flasks. Two solutions, one of sodium hydroxide, pH 12, and the other a silica solution, pH 12, were mixed in varying proportions to yield solutions of differing silica concentrations, sample 1 containing only sodium hydroxide, and sample 6 containing only silica solution. After two days, the yellow color was quite pronounced in all but sample 1, and increased in intensity with higher silica concentration. After three days, aliquots were taken from each solution, the silica removed by precipitation and dehydration, and the filtrates analyzed for iron via the standard thiocyanate colorimetric method. The amount of iron detected is plotted vs the amount of silica in solution (silica as percent by weight SiO_2) in Figure 22. An identical series gave similar results after 7 days (B in Fig. 22). At the time of

1. Two hundred gms of Glory stone (sample 3, Table 6) of uniform size, passing a standard No. 6 sieve and retained on a No. 10 sieve, were placed in each of a series of seven bottles. Exactly 200 ml of silica solution was added to each sample. Two blanks were prepared by placing a quantity of pure, crushed calcite rhombs and pure, crushed dolomite rhombs in equilibrium with the same silica solution. A third blank was prepared to check the stability of the silica solution.

The silica concentration was determined at intervals by removing a 50 ml aliquot from a different bottle each time and analyzing for SiO_2 gravimetrically.

The silica concentration in the solutions in

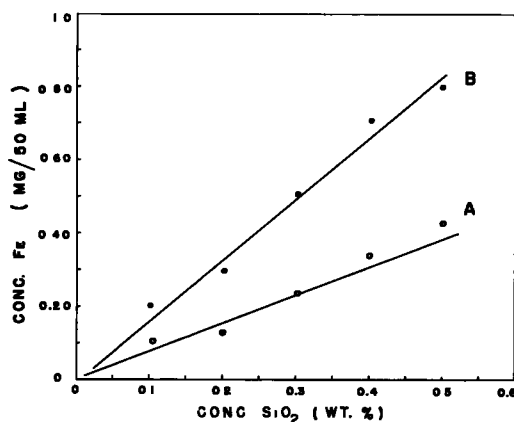


Figure 22. Increase in Fe concentration of solutions in equilibrium with carbonate rock (Glory No. 3) plotted vs the SiO_2 concentration of the solution after 3 days, A, and after 7 days, B.

this report, similar determinations of the aluminum in solution have not been made. The results to date, however, definitely indicate that certain carbonate rocks are involved in "activity" with silica in a high pH environment. The pH of portland cement paste in equilibrium with distilled water is 12.

For an excellent review of the chemistry of the compounds in cement paste, the reader is referred to the review by H. H. Steinour (24), and the references contained therein. At the time of the first presentation of this report, the authors were criticized for suggesting that silica may be "mobilized" in a cement paste environment and finally, after migration, reside preferentially in aggregate particles. It should be stressed that the discussion in Mr. Steinour's review deals with the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system as such. In this case, the mobility of the silica is markedly decreased by any increase in lime concentration (24). The presence of alkali in cement paste, however, may function to free more silica. The solubility of $\text{CaO} \cdot \text{SiO}_2 \cdot \text{aq}$ and similar compounds is not completely understood (24) and the many equilibria which are involved in a consideration of the chemical "activity" of cement paste render the situation more complicated. The fact that silica can be extracted from cement paste with water was demonstrated as follows.

Bars of hydrated portland cement paste supplied by Bert Myers, of the Iowa State Highway Commission, were reduced to chips by hammering. Three hundred grams of a given size fraction (passing No. 10 sieve, retained on No. 32 sieve) were placed in six polyethylene bottles, 50 gms in each and distilled water added. After several hours, the pH of the resulting solutions was 12. The bottles were stoppered and agitated for 12 hours. The agitation caused considerable abrasion and finer particles were formed. The solids were then separated by filtration and the filtrates combined for evaporation and analysis. The combined filtrates yielded 0.026 gms of SiO_2 .

The authors feel that it is not impossible for silica originally contained in the cement paste to assume some migratable form enabling it to seek a site of greater stability. Furthermore, the results of the preliminary experiments reported herein are taken to indicate that certain types of carbonate rock, when present as aggregate in concrete, may afford such a site of greater stability.

Further quantitative studies of the observed phenomena are being continued, and more data will be presented in the future.

SUMMARY OF OBSERVATIONS

1. When present in the affected concrete samples which were examined, those carbonate rocks which contained clay, a high percentage of insoluble residue, and high magnesium content were characterized by marked reaction rims.
2. The reaction rims are not merely staining phenomena but are definitely the result of chemical activity and accompanying transfer of material.
3. Pure limestones (that is, carbonate rocks with low percentage of insoluble residue and high calcium content) do not develop reaction rims and appear to be relatively inert.
4. The fact that certain impure carbonate rocks in silica solution at pH 12 develop definite zones or rims of more insoluble material while silica is removed from solution and other ions introduced into the solution, may be taken to indicate that the rims in affected concrete are developed via a similar transfer.
5. The nature of the chemical activity postulated in the foregoing would imply that the physical characteristics of the aggregate, such as effective porosity and pore-size distribution, are critical and must be considered in an ultimate evaluation of potential aggregate.

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