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Treatment of Carbonate Rocks with a Vaporous Mixture of $(\text{CH}_3)_2\text{SiCl}_2$ and CH_3SiCl_3

By CARL L. HILTROP and JOHN LEMISH

Abstract. Preliminary investigations concerning the treatment of dry carbonate rocks with some derivatives of silane in the vapor state are described. The treated rocks appear similar to affected aggregates observed in some inferior concretes.

Considerable research in recent years has been aimed at discovering those properties of a carbonate rock which are deciding factors in determining whether or not that rock will prove to be a good concrete aggregate. One of the earliest investigations of this subject was that by Laughlin (1928). Others of significance are those of Sweet (1948) and Mather (1952; 1953).

Investigation concerning the suitability of carbonate rocks of Iowa for use as aggregate in the construction of concrete highways was instituted by Dorheim (1950). The work was continued by Roy, Thomas, Weissman, and Schneider (1955), who concluded that high absorption and presence of swelling type clay favor reactions between cement and aggregate which produce distress.

Bisque and Lemish (1958; 1959), while investigating sections of Iowa highways which had proved unsatisfactory in service, noted the presence of "reaction shells" on the periphery of the carbonate aggregate. Subsequent laboratory studies led to the conclusion that these reaction shells were richer in silica than was the original host rock. Thus it seemed that silica, in some mobile form, had migrated from the siliceous cement paste and had been deposited within the carbonate aggregate forming a less soluble, more siliceous "reaction shell". As partial proof of this thesis, reaction shells were grown in carbonate rocks which were quite similar to those observed in the aggregate of unsatisfactory highways. These reaction shells were produced in two ways:

1. Rock specimens were placed in a water solution of sodium metasilicate.
2. Rock specimens were placed in laboratory-prepared concrete bars which were subsequently placed in a water bath at slightly elevated temperature.

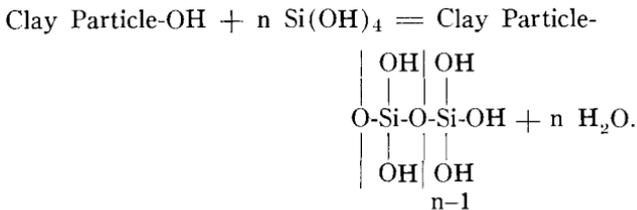
Furthermore, it was observed that those rocks which were relatively impure (i.e., contained significant amounts of insoluble material and illitic clays), were most susceptible to shell growth.

Hiltrop and Lemish (1959) investigated the chemical and physical properties of aggregate from eight quarries. Sufficient data were available concerning the serviceability of highways constructed using aggregate from these various quarries, that correlations could be drawn between chemical and/or physical properties and serviceability. In nearly every case, among those specimens studied, those rocks known to have a poor service record were found to contain significant quantities of illitic clay.

In reviewing the above work, the authors of the present paper reasoned that since mobile silica was capable of being absorbed readily from either water solution or from hardened concrete paste by certain carbonate rocks, it would be interesting to see whether or not a similar reaction would take place when those rocks were placed, dry, in an atmosphere of vaporous silicic acid. The ease with which this experiment was performed and the rather startling product obtained, led to the decision to treat several specimens with a vaporous mixture of $(\text{CH}_3)_2\text{SiCl}_2$ and CH_3SiCl_3 and to examine the resultant rock. The reader should be well aware that this is a preliminary report. The problems revealed by treatment of carbonate rock specimens with these reagents have not been exhaustively studied. This preliminary report is submitted in the hope that other investigators having similar interests will find the phenomena described here useful.

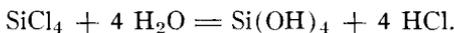
THEORY

Because rocks which contain a higher portion of argillaceous material absorb silica (from solution and from concrete paste) more readily than do pure carbonates, one might reasonably postulate the occurrence of a condensation polymerization of the following type.



If, in fact, a condensation of that nature were taking place one might expect a dry argillaceous carbonate rock to react with vaporous silicic acid in a similar manner.

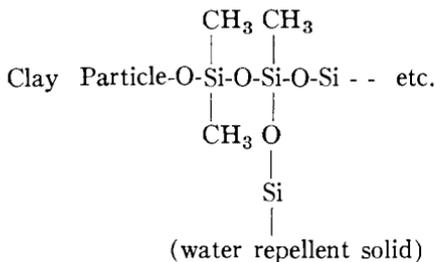
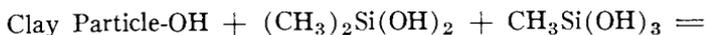
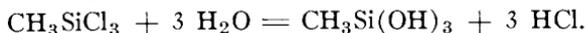
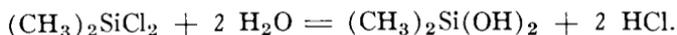
A supply of vaporous silicic acid is readily generated by allowing SiCl_4 (boiling point 57.6°C) to volatilize and to be hydrolyzed by the water vapor in the atmosphere (Rochow, 1951).



The vaporous silicic acid thus formed would be available to undergo

condensation with the argillaceous material contained throughout the rock. Since the vaporous silicic acid possesses 4 reactive functional groups, one would expect to get a great deal of cross-linking with resultant growth of a three-dimensional network of hydrated SiO₂.

In a similar vein, one might expect the clay particles contained throughout a rock to condense with certain volatile organic derivatives of silane. In particular, a mixture of dimethyldichlorosilane and methyltrichlorosilane could be expected to form a three-dimensional polymer. If such a polymer were to form, the resultant "treated" rock could reasonably be expected to possess quite different properties than it possessed in its original condition. For example, it would be reasonable to expect that the hydrophobic methyl groups on the resultant silicone polymer would impart some water repellency (Rochow, 1951).



EXPERIMENTAL

The procedure and equipment used to impregnate the rock specimens with the various silanes were quite simple but effective. An evaporating dish containing 20 to 25 mls. of silicontetrachloride or 20 to 25 mls. of an approximately equal volume mixture of dimethyldichlorosilane and methyltrichlorosilane was placed at the bottom of a glass desiccator. The porcelain desiccator plate was placed in position, and the rock specimens to be treated were positioned on top of that. A vacuum type lid was placed on the desiccator with the vacuum vent open to atmosphere. The desiccator with its contents was then placed in a hood and allowed to stand for several hours or for several days, as desired. Caution is suggested when handling these materials since hydrochloric acid is a by-product of the hydrolysis.

Technical grade reagents were ordered from Dow Chemical, Midland, Michigan.

RESULTS

Silicon Tetrachloride

Table 1 shows the gain in weight by carbonate rocks placed in an atmosphere of silicon tetrachloride. The three specimens, which consisted of rock chips approximately one inch in diameter, were oven dried overnight before treatment was begun. They were also oven dried each time before weighing.

Table 1
Weight Gained By Rock Specimens

Time in Days	Specimen Number		
	1	2	3
0	6.728	10.414	10.143
1	6.738	10.449	10.184
4	6.744	10.473	10.212
7	6.787	10.556	10.321

At the end of the fourth day the chips were placed in an atmosphere of $(\text{CH}_3)_2\text{SiCl}_2$ and CH_3SiCl_3 and the gain in weight was noted three days later.

Specimens which had been treated with SiCl_4 were found to effervesce much more slowly when placed in 4 normal hydrochloric acid than did untreated specimens. After one day's treatment, a very noticeable insoluble reaction shell was apparent. At the end of two days, the insoluble reaction shell had migrated farther into the rock. At the end of four days, the complete rock was found to be transformed to a much more insoluble condition than it had been originally.

It is interesting to note that specimen number 1 was the purest carbonate of the three rocks and also showed the least gain in weight. Furthermore, pure carbonates remain fairly soluble in HCl after treatment, while more impure rocks form a very obvious insoluble reaction shell.

Dimethyldichlorosilane and Methyltrichlorosilane

Figure 1 shows a piece of untreated argillaceous limestone on the left and a similar piece of rock on the right which has been treated. The water repellency is apparent. The water-surface contact angle is estimated to be about 110 degrees. The striking thing is that the water repellency effect is not limited to the exterior surface only. After approximately four hours treatment, rocks of about one inch diameter were broken open and were found to be water repellent throughout.

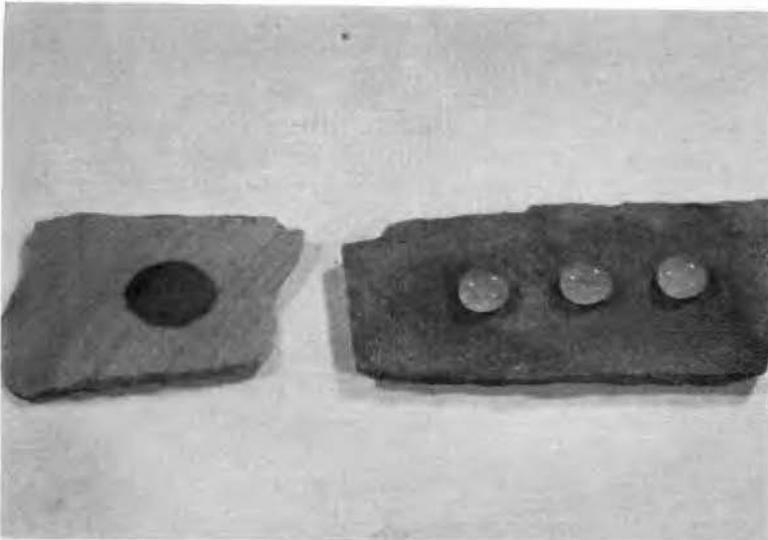


Figure 1. Water repellency exhibited by treated limestone at the right. Untreated specimen at the left.

Figure 2 shows the result (left beaker) of placing a piece of argillaceous limestone in 4 normal HCl. The picture was taken about one hour after immersion. The beaker on the right contains a comparable piece of rock which was treated with the vapors of the organosilanes. The treated rock had been in the 4 normal HCl for two days when the picture was taken. In the case of the treated

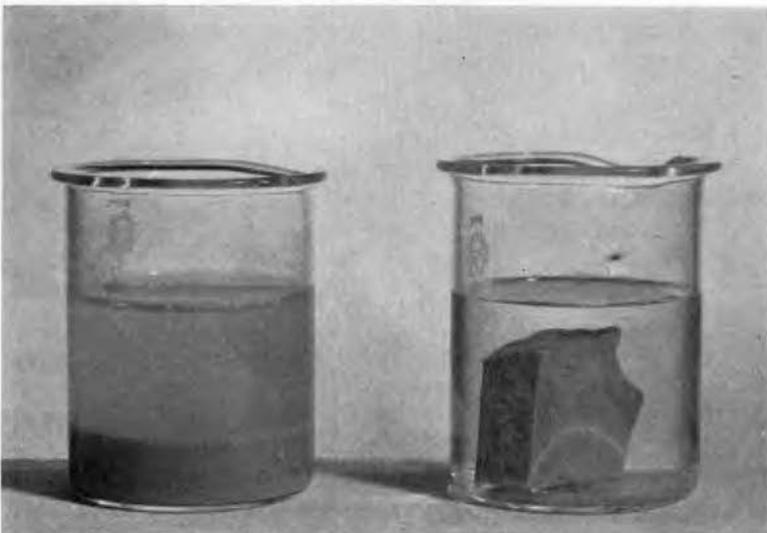


Figure 2. Resistance to leaching by hydrochloric acid is demonstrated by treated limestone at right. Untreated specimen at the left.

specimen, the carbonate was leached away very slowly leaving the insoluble argillaceous material in its original three-dimensional configuration.

Figure 3 is a photomicrograph of the insoluble material remaining after a treated carbonate rock has been leached several hours in concentrated HCl. Note the clean, sharp casts of dolomite rhombs.

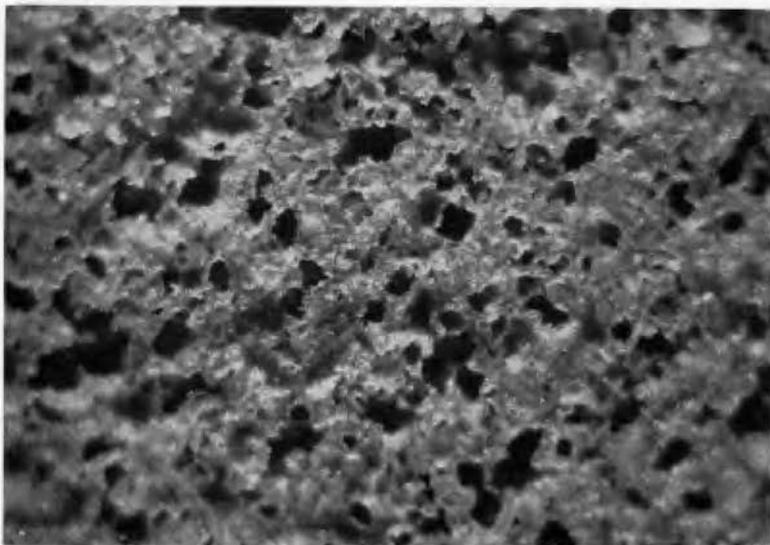


Figure 3. Photomicrograph of treated limestone after long leaching in concentrated hydrochloric acid. x50.

It is interesting to note (Table 1) that rocks which were treated for four days with vaporous SiCl_4 and then with the vaporous organosilanes continued to gain weight. Furthermore, they, too, became fully water repellent throughout.

Figure 4 illustrates the effect of treating hardened concrete with the vaporous organosilanes. The specimen on the right demonstrates the water repellent effect. When broken, it was found to be water repellent throughout. A treated specimen of concrete was subjected to leaching in strong hydrochloric acid. It was observed to be quite resistant to the acid as contrasted to a non-treated specimen which readily effervesced and disintegrated. The final results of this acid leaching were similar to those of the limestone specimens illustrated in Figure 2.

DISCUSSION

The fact that the carbonate can be completely leached away from an argillaceous limestone (refer again to Figure 2) which has been treated in the organosilane, leaving the insoluble residue with all of its original bedding, its structure, its texture, and other three-dimen-

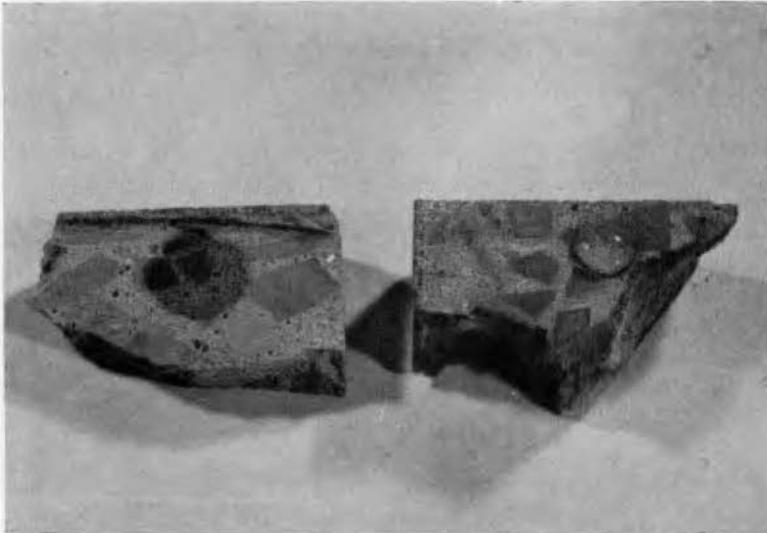


Figure 4. Water repellency exhibited by treated concrete at the right. Untreated specimen at the left.

sional characteristics preserved, argues in favor of the polymerization postulated earlier. It would seem that the small particles of insoluble material which were in the original rock have been linked together by the growing three-dimensional siloxane. The authors believe that all the results obtained here are further corroboration of the original arguments put forth by Bisque and Lemish (1958; 1959) concerning the growth of reaction shells in inferior concrete.

The research is to be continued in two directions.

1. Samples of neat cement paste and of various concretes, as well as carbonate rocks, are being treated and examined. Freeze-thaw tests will be run. Specimens will be tested for compressive strengths. The effect of this treatment on alkali-aggregate reactivity (Mielenz and Greene, 1947) and on carbonate silicification (Bisque and Lemish, 1959) will be examined.
2. Microscope and X-ray studies will be conducted in an effort to learn more of the exact nature and distribution of clay particles in a carbonate rock. Specimens will be treated and the carbonate subsequently leached. Thin sections and X-ray mounts will then be prepared from the remaining insoluble material. Attempts will also be made to prepare thin section specimens by use of the microtome.

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