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Silica behavior in aggregates and concrete

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SILICA BEHAVIOR IN AGGREGATES AND CONCRETE

by

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The work presented here is a continuation of that done by the author, and others, in an attempt to better understand and to better differentiate between "good" and "bad" carbonate aggregate.

A large part of past work has centered about the growth of "reaction shells". Two hypotheses have been proposed for their growth, both of which involve migration of silicate ion.

A method of rock sampling and refluxing is described. Refluxing is done in order to hasten reaction. Some of the results of preliminary reflux experiments corroborate, and some negate, the proposed methods of shell growth.

A consideration of shell growth led to the treatment of carbonate rocks with vaporous organosilanes. This treatment, in turn, led to an application for patent. That treatment and the present status of that patent are described.

Further consideration of shell growth and the proposed "dedolomitization" theory led to the proposal of a method for determining calcite to dolomite ratio in a carbonate rock. That method is described.

Suggestions are made for continuing the work.
I. INTRODUCTION

A. Nature of Program

The study presented here was carried on as part of a research program sponsored by the Iowa State Highway Commission. The purpose of this program is to delineate those properties, geological, chemical, or physical, of a carbonate rock which determine whether or not that rock will serve satisfactorily as coarse aggregate for concrete highway construction.

Coarse aggregate for concrete highways can consist of igneous gravels or crushed stone particles, or combinations of these two materials. One hundred per cent of these particles is required to pass the 1 1/2 inch sieve; zero per cent is allowed to pass the No. 4 sieve. This coarse fraction comprises some 40-50 per cent of the concrete by volume.

If that coarse fraction is composed of such a material that it does not possess the necessary physical qualities, or if it undergoes some deleterous chemical reaction once it is placed in the environment of the cement paste, it will lead to premature deterioration of the concrete highway.

Records compiled by the Iowa State Highway Commission show that highways constructed using crushed stone from certain quarries demonstrate unusually good service records whereas highways constructed using crushed stone from other quarries demonstrate unusually poor service records. Realization of this fact led to the institution of the present research program. Such studies are of particular interest in areas where
lack of sufficient igneous gravels necessitate the use of crushed carbonate rock. The state of Iowa is, for the most part, such an area.

B. Nature of Thesis

Several publications have been forthcoming as a result of the limestone investigations carried on in the geochemical laboratories of the Geology Department, Iowa State University. It is the purpose of this thesis to:

1. Present a review of those investigations, as well as a review of the work of others in the field.
2. Present recently collected data.
3. Coordinate the information presently available, and suggest the direction of future research.
II. REVIEW OF CARBONATE AGGREGATE PROBLEM

Literature concerned with the behavior and suitability of carbonate rocks as concrete aggregate is not extensive. One of the earliest investigations of this subject was that by Laughlin (1928). Other early investigations of significance are those by Sweet (1948) and Mather et al. (1952, 1953).

Investigations concerning the suitability of Iowa carbonates as concrete aggregate were inaugurated at Iowa State College by Dorheim (1950). It had been recognized that certain carbonate rocks, when used as aggregate, did not always behave as indicated by standard acceptance tests. The purpose of that investigation was to find, through consideration of some of the geologic aspects, new criteria for the selection of limestone aggregates to be used in concrete. From the Parallelism between the service record and the clay content Dorheim suggested that the presence or absence of clay might be used as an additional guide upon which to more discriminatingly select limestone aggregates.

The work was continued by Roy, Thomas, Weissmann, and Schneider (1955). Of special interest, in their investigations, were the Mississippian rocks quarried in the vicinity of LeGrand, Iowa, which have a poor service record when used in concrete highway. The study of concrete cores taken from satisfactory and from distressed pavements indicated that fresh stone gave satisfactory service, whereas, weathered stone
produced distress. The adsorption capacity, in itself, did not indicate unsatisfactory stone.

Bisque and Lemish (1958, 1959) investigated some of the chemical properties of carbonate rocks as related to durability of concrete. Carbonate rocks of Devonian age were sampled and rocks from the Glory quarry, which have an unsatisfactory service record as aggregate, were used as a basis for comparison. While investigating sections of Iowa highways which had proved themselves unsatisfactory in service, they 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.

Lemish, Rush, and Hiltrop (1958) reported on some of the physical properties of carbonate aggregate as related to the durability of concrete. Devonian rocks from the Cedar Valley formation were sampled on a bed-by-bed basis in four quarries, one of which was the condemned Glory quarry. It was concluded that impure carbonate rocks characterized by high residue and high clay content were poor aggregate. Preliminary investigations of the pore-size distribution present within a rock indicated that it might be of importance in determining its suitability for concrete aggregate. This suggested a more detailed study of the pores and pore-size distribution possessed by a carbonate rock. Such a study was reported by Hiltrop and Lemish (1959) who investigated some of 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, so that correlations could be drawn between chemical and/or physical properties and serviceability. Hiltrop (1958) had proposed a method, based on conditional probabilities whereby the effect of the various characteristics of a carbonate rock on serviceability could be evaluated. Among those specimens studied, the probabilities indicated that high illitic clay content and low calcium to magnesium ratio (i.e., high dolomite content)
correlated well with "poor" service record.

Bisque and Lemish (1961) reported results of experiments on test bars which had been made of both "acceptable" and "non-acceptable" carbonate aggregate. These test bars were alternately soaked in distilled water at 140°F and dried at room temperature. That wetting and drying was continued for 4 months. At the end of that time, growth measurements were made and compressive strengths were determined. Comparison was made with a similar set of specimens which had not been cycled, wet and dry. Inspection showed that reaction shells, similar to those observed in affected concrete, had grown in the nonacceptable aggregate. Furthermore, comparison showed that bars made with nonacceptable aggregate resulted in:

1. No expansion in excess of that experienced by comparison bars which had been made with acceptable aggregate.

and

2. A definite decrease in the amount of compressive strength gained during hydration.

Additional tests on aggregate specimens, which had reacted with cement paste, showed an increase in silicon content of aggregate with no increase in soda or potash.

The above results showed that shell growth is deleterious to hardened concrete. The authors reported that results further confirmed their postulated mechanism of shell growth. The authors postulated a "tying together", or polymerization, of clay particles according to the following mechanism.
Other investigators have postulated a "dedolomitization" reaction (Swenson and Gillott 1960, Chaiken and Halstead 1960) in an attempt to explain the deleterious role played by some carbonate aggregates in concrete. Dedolomitization is depicted as involving the following reaction:

\[
\text{Ca}_{1-y}\text{Mg}_y\text{CO}_3 + 2\text{OH}^- = \text{Ca}_{1-y}\text{Mg}_y\text{zCO}_3\text{ l-z} + z\text{Mg(OH)}_2 + z\text{CO}_3^-
\]

Dolomite I base Dolomite II Brucite

Dedolomitization, according to the above authors, is accompanied by weakening of the aggregate and/or of the cement paste.

Harwood (1960) placed several carbonate rock specimens, each of which were representative of different lithologic units, in cement paste and allowed the paste to harden. These hardened concrete specimens were then placed in a constant temperature bath, 55°C, and allowed to remain for three months. At the end of that period, 1 gram samples were collected at various distances from the cement-aggregate interface and chemical determinations made. A hypothesis was presented to explain the variations found in the aggregate and cement paste after their
interaction. It was postulated that the variations found, after interaction, could be explained on the basis of the pH and concentrations of available silicate, calcium and magnesium ions on both sides of the interface. If the concentration of reactive silica were higher in the cement paste than in the aggregate, silica was postulated to move into the aggregate; if it were lower in the cement than in the aggregate, the opposite would occur. Basicity was postulated as decreasing inward, from the interface into the aggregate.

In the instance where the reactive silica concentration is greater in the aggregate than in the cement, the net effect was postulated to be the movement of silica from the aggregate into the cement. In this instance, too, a reaction shell was observed in the aggregate and was postulated to form as follows. In the shell zone of the aggregate the solution of quartz by the alkali from the cement will generate a solution saturated in silicate ion. In such a saturated solution, both precipitation and solution are occurring simultaneously. However the concentration of silicate ion is higher in the aggregate than in the cement and, thus, silicate ion migrates out into the paste. The shell zone is cemented together by the silica that is precipitated in the aggregate, but the net affect is to reduce the amount of silica in the aggregate shell zone.
III. PRESENT STATUS OF THE PROBLEM

A. General Statement

When any type of rock is placed in cement, it would be reasonable to expect various reactions to be initiated. A rock, by definition, is an aggregate of minerals; which minerals were thermodynamically stable under the conditions at which the rock formed — and thus did form.

In a similar manner, the minerals which comprise dry cement are those which were thermodynamically stable under the conditions at which the raw products were burned to form cement. When the rock is quarried and removed from its environment of stability, and the dry cement is wet, and the two are mixed — one would expect various reactions to be initiated between the several components of the aggregate and cement. The direction of those reactions (as does the direction of any reaction) depends on $\Delta F$, (which determines the equilibrium constant), on temperature, on pressure and on concentration of reactants and products. Rate of reaction is, of course, another matter. Rate being a function of the rate constant as well as relative concentrations.

Which of the reactions, taking place in concrete, are doing so relatively rapidly and are producing deleterious effects?

At one time or another, all the major components of the aggregate (and some of the lesser components) have been called on as the initiators of deleterious reactions.
One of those major components, often cited as the source of material entering into deleterious chemical reactions, is silica in some "reactive" form. The reactive aggregates are usually believed to be those containing opal, chalcedony, or certain glassy or very fine-grained volcanic rock. Powers and Steinour (1955) suggest, for example, that opal can be considered a highly condensed silica-gel. They say, further, that such a material has a large surface area (mainly internal surface area) and is, thus, susceptible to hydrolysis by the OH$^-$ ion available from the cement paste. The newly formed reaction product has a tendency to absorb water and increase in volume. Because the reaction product is confined by the comparatively rigid cement paste, this tendency of the reaction product to increase in volume generates internal pressures within the concrete. When such pressures are of sufficient magnitude to exceed the tensile strength of the surrounding cement paste, cracking and expansion of the concrete occur. If more water and/or alkalies are available, the reaction proceeds to a greater extent, producing a gel-like product which can be seen filling previously formed rocks.

The above type of reaction is referred to as the alkali-aggregate reaction. For a review of the fundamental research done on that problem see Halstead and Chaiken (1958).

Another postulated form of reactive silica, present in carbonate rocks, is that silica present in clays. Since some clays are known to readily imbibe water and to enter into ion
exchange reactions, it seems reasonable that it might also enter into a similar "alkali-aggregate" reaction or, perhaps, into a polymerization such as that postulated by Bisque and Lemish (1958). A "disordered" clay was hypothesized as possibly being most reactive. Harwood (1960) suspects all silicate minerals present in the aggregate to enter into reactions which lead to shell growth. Quartz, amorphous silica and clay particles are mentioned.

A second major phase of carbonate rock which has, more recently, been blamed for concrete deterioration, is the carbonate phase itself. That phase is composed, for the most part, of either pure dolomite (CaMg(CO₃)₂) or pure calcite (CaCO₃), or mixtures of those two minerals, either of which may have compositions slightly different from the ideal compositions presented here.

Swenson and Gillott (1960) investigated the excessive expansion and cracking of concrete, which was made using an argillaceous dolomitic limestone from Kingston, Ontario, as aggregate. They proposed as a tentative conclusion that rocks composed of near equal proportions by weight of dolomite and calcite may be regarded as suspect and that it seemed possible that a connection existed between the expansive reactivity and the dedolomitization reaction.

Sereda (1960) has investigated the absorption of water by aggregates. He reports that they are capable of exhibiting absorption hysteresis curves and postulates swelling of
aggregate as a result of the hysteresis effect.

The dedolomitization reaction, as presented by Chaiken and Halstead (1959), involves the reaction of OH− ion with dolomite and subsequent formation of solid brucite and a new dolomite. One wonders if it is not just as plausible to postulate a similar reaction for an impure calite.

One of the minor components of aggregate which has received a great deal of consideration is sulfate ion. Lamar and Shrode (1953) investigated the presence of various water soluble salts in several Illinois limestones. They reported some of their specimens to contain as much as 0.1% of SO₄²⁻ by weight. Their conclusion was that most of that sulfate occurred as intergranular solid calcium sulfate with magnesium sulfate possibly occurring in the same manner.

It is believed that sulfates dissolved from aggregates and enclosed in portland cement can cause expansion and disintegration of concrete through alteration of the aluminates and silicates of the cement. Calcium sulfoaluminate results when sulfate concentration is low. Gypsum crystals result when sulfate ion concentration is higher.

B. Silicate Studies

1. Problem of silicate behavior

A good portion of the work, reported on the carbonate aggregate-cement paste reaction, suggests that shell growth is a function of the number of "reactive" sites available in the silicates present. For example "disordered" clays are hypothesized
as being reactive. It would appear that if one had a high proportion of disordered clays, this would lead to a high proportion of short chained polymers in solution if the solid clay mass were placed in water, and the water allowed to become saturated with silicate. Perhaps, then, examination of the saturated solution above an argillaceous carbonate would lead to evidence indicative of that rock's potential serviceability as concrete aggregate.

Considerations of this nature make it appear worth while to present a brief resume of the solution chemistry of silicon.

2. Review of literature

Roy (1945) reviewed both the geologic literature and chemical literature, available at that time, concerning the form of silicate ion in solution. He pointed out that geologists, in general, believed that silicon was transported in solution in what was vaguely termed the colloidal state. This belief was based on a paper by Kahlenberg and Lincoln (1898). Chemical literature, on the other hand, advocated SiO$_3^{2-}$ as the species in solution, such a species had been proposed in a series of papers by Harman (1925, 1926, 1957).

Roy further pointed out that additional research with respect to the actual molecular character of the dissolved silica and the ways in which silica may be precipitated was desirable.

Since 1945, a large volume of literature, which concerns itself with silicate ion in solution, has accumulated. One of
the foremost geochemists working in the field is Krauskopf (1959). He has summarized a good portion of the more recent findings on the solubility of amorphous silica. He points out that solubility of SiO$_2$ is a straight line function of temperature. Between 0$^\circ$ and 200$^\circ$ C the solubility increases from about 100 ppm to about 900 ppm. Furthermore he shows that the equilibrium concentration arrived at is the same regardless of whether solid silica is being put into solution, or a supersaturated solution is caused to precipitate out. In solutions containing more silica than the equilibrium concentration, the excess silica gradually polymerized to form colloidal particles.

Greenberg (1955), too, writes of the polymerization of silicic acid. He reports that when acids, or some salts, are added to a sodium silicate solution, the pH is lowered and the viscosity of the mixture increases until a gel is formed. During this transformation, colloidal and chemical changes are occurring - any monomeric silicic acid present polymerizes to form polysilicic acid particles.

Earley and Fortnum (1959) reports Raman spectral data show silicate ion to be SiO$_2$(OH)$_2$$^-$.$^2$. Also, calculations based on estimated equilibrium constants indicate that hydrolysis and polymerization would be significant in basic media. Therefore, a spectral line at 1040 cm$^{-1}$ was interpreted as resulting from a species other than monomeric ion of dinegative charge. Since the constants indicate that polymerized species are more likely than hydrolyzed monomer, he concluded that this line at 1040
15 cm\(^{-1}\) can be assigned to a polymeric ion.

Goto (1956) reviews the findings of several different workers and comments on the disagreement that exists among their conclusions concerning the effect of pH on polymerization of silicic acid in water. It is his belief that disagreement arises because the assumption is made that polymerization proceeds to the same equilibrium state regardless of pH.

3. Approaches to problem

In order to gain some knowledge as to the actual status of silicate, (both solid and soluble), in the carbonate aggregate, the author proposes the following three approaches.

The first proposal has to do with the solution chemistry of pure sodium metasilicate. Possibly a better understanding of silicate in solution might be forthcoming if the ion species were considered from a statistical point of view. At the same time, such a view might shed some light on the carbonate aggregate-cement paste reaction.

Consider, as an example, sodium metasilicate, the infinitely long, linear condensation polymer. Suppose that this straight chained polymer has been placed in solution and partially degraded by base catalyzed hydrolysis.

Now suppose that after some appropriate length of time the hydrolytic reaction is quenched, our problem is to provide a description of the various ionic species present in solution in the reaction pot.
Suppose that the terminal hydroxyl group of a molecule has been selected at random and that we wish to know the probability that this molecule is composed of exactly \( x \) units.

\[
\begin{array}{ccc}
\text{O} & \text{O} & \text{O} \\
\text{HO-Si-O-Si-O-Si-O} & \ldots \ldots \ldots \ldots & \text{O-Si-OH} \\
\text{O} & \text{O} & \text{O} \\
1 & 2 & 3 \ldots \ldots \ldots \ldots x-1 & x
\end{array}
\]

The probability that the oxygen of unit number 1 is bonded to a silicon in unit number 2 is equal to \( p \), by definition. The probability that the oxygen of the second unit is bonded to a third silicon is again \( p \). The probability that this sequence continues for \( x-1 \) linkages is the product of these separate probabilities, or \( p^{x-1} \). For, as Mood (1950) states, "If the constituent events of a compound event are mutually independent, the probability of the compound event is equal to the product of the probabilities of the constituent events." Then \( p^{x-1} \) is the probability that the molecule contains at least \( x-1 \) linkages, or at least \( x \) units. The probability that the \( x \)-th silicon unit is unreacted, thus limiting the chain to exactly \( x \) units, is \((1-p)\). Hence the probability that the molecule in question is composed of exactly \( x \) units is given by

\[
n_x = p^{x-1}(1-p) .
\]

If none but linear open chain polymer molecules are present, which we assume to be the case, then obviously the prob-
ability $n_x$, that any molecule selected at random is composed of $x$ units must equal the mole fraction of $x$-mers.

The total number of $x$-mers is given by

$$N_x = N(1-p)p^{x-1}, \quad (1')$$

where $N$ is the total number of molecules of all sizes. If we let $N_0$ represent the total number of units, we shall arrive at

$$N_x = N_0(1-p)^2p^{x-1}. \quad (2)$$

For if we start with an infinitely long chain containing $N_0$ units and cleave the fractional part, $(1-p)$, of the bonds between the units, (where each cleavage results in the production of two new $-\text{OH}$ groups), it is obvious that the number of molecules, $N$, will equal $1/2$ the number of $-\text{OH}$ groups. Now

$$\text{No. of } -\text{OH groups} = 2N_0(1-p).$$

But

$$1/2 \text{ No. of } -\text{OH groups} = \text{No. of molecules} = N.$$

Therefore

$$N = N_0(1-p). \quad (3)$$

If this value of $N$ is substituted into Equation (1'), one arrives at desired Equation (2).

Because of the occurrence of the distribution described by Equation (2) under a wide variety of controlling circumstances,
it is designated as the "most probable distribution".

Since the molecular weight of each species is directly proportional to \( x \), the weight fraction can be written

\[
w_x = \frac{xN_x}{N_0}.
\]

Substituting from Equation (2), one has

\[
w_x = x(1-p)^2p^{x-1}.
\] (4)

Figures 1 and 2 demonstrate the difference in the two functions \( N_x \) and \( W_x \) for the same degree of reaction \( p \).

Thus, functions have been derived for describing the weight fraction distribution (Equation 4) and the mole fraction distribution (Equation 2), present in a partially degraded sodium silicate mixture, based on the principle of equal reactivity in the kinetic sense that all functional groups of the same chemical type are equally susceptible to cleavage regardless of the size of the molecule to which they are attached.

The above hypothesis is presented in order to illustrate the approach one might use to describe silicate solutions. In the case where the ions in solution are being furnished by dissolving naturally occurring solid silicates, one might expect to find branched and cross-linked polymeric ions. In that case, the distribution function would be considerably more complicated than the one derived above. For a complete text on the principles of polymer chemistry see Flory (1953).
Figure 1. Mole fraction distributions for several extents of reaction p.

Figure 2. Weight fraction distributions for several extents of reaction p.
\[ N_x \]

\[ \omega_x \]

\[ p = 0.95 \]

\[ p = 0.98 \]

\[ p = 0.99 \]
Following is a very brief outline of an experimental approach which one might use to verify or disprove the validity of the hypothesized "most probable distribution" as applied to sodium metasilicate ion in solution. That is, a method for testing the validity of Equation 2.

Equation 2 is:

\[ N_x = N_0 (1-p)^2 p x^{-1} \]

where \( p \) is the degree of polymerization.

Alexander (1953 and 1954) describes a method for following the kinetics of polymerization of monosilicic acid by use of freezing point depression. Thus, we have a method of evaluating \( p \) in Equation 2. \( N_1 \), (i.e., number of monomers present), can be obtained by the method of Weitz, Francke and Schuchard (1950). They reported that monomeric silicic acid reacts with molybdic acid completely, in dilute solution, within 75 seconds while higher silicic acids react only after about ten minutes. That report was confirmed by the work of Richardson and Waddams (1954).

Thus \( N_1 \) can be calculated, if we know \( p \), by use of Equation 2. At the same time \( N_1 \) can be obtained experimentally by the 75 second molybdate method. If the calculated value and the experimental value agree, this would verify Equation 2 and at the same time lead one to reason that probably naturally occurring silicates, in solution, obey some distribution function.
A second, and more direct approach, is to examine the silicates in a water solution that has been allowed to equilibrate with the aggregate in question. It has been shown that the species of silicate, in solution, is dependent on the previous history of the sample. Experiments are described, in a later section, which give values for 1-total silicon in solution. And 2-percent molybdate reactive silicon.

A third approach is through the use of vaporous organo-silane materials. It was believed that these studies might lead to some knowledge of the availability of "reactive" sites in the argillaceous aggregate. The experiments and results of these silane studies are presented in a later section.
IV. SILICATE INVESTIGATIONS

A. Representative Sampling

Since the initial observation of the presence of "reaction shells" in inferior aggregate (Bisque and Lemish, 1958), a considerable amount of effort has been expended in an attempt to determine what chemical changes accompany shell growth in the aggregate. When one attempts to make that determination he is immediately confronted by two problems: 1) the natural inhomogeneity of a carbonate rock, 2) the long length of time required to grow reaction shells in the laboratory.

Plate 1, which is a photograph of a carbonate rock cube in which a reaction shell has grown, is presented to better illustrate the inhomogeneity of some of the rocks examined. The thin, feathery, white particles standing out, after acid etching, are composed of a fiberous variety of quartz. It is apparent that taking very small samples for analysis may lead to erroneous conclusions.

In order to further illustrate the inhomogeneity of some carbonate rocks, four 1 gram samples were selected from a hand specimen of a typical aggregate and analyzed for SiO₂. The results varied within a range of about ± 4%.

Bisque and Lemish (1958, 1961) tried to circumvent the first problem by using a large weight of sample composed of many small chips of rock. He selected, in every case, two similar samples and analyzed one without reacting with cement paste and
Plate 2. Chip of Glory 2, after re-fluxing and subsequent acid etching.

Plate 1. A carbonate aggregate cube after acid etching.
the other after reaction in the cement paste environment for a period of three months. By selecting his samples in this manner, he hoped to lessen the probability of misinterpreting the data obtained because of the natural inhomogeneity of the rock. Bisque concluded that silica was being absorbed by the aggregate.

Harwood (1960) selected five 2 x 2 x 2 inch cubes, one from each of five different lithologic units, and placed them in concrete test bars. These bars were then placed in a constant temperature bath and allowed to stand three months. After that period, the test bars were sawed in half and one gram samples were obtained, by use of a dentists drill, at various distances from the aggregate-paste interface. From the data obtained in this manner, a hypothesis was presented to explain shell growth. That hypothesis was based on two basic postulates 1) the difference of $\text{OH}^-$ concentration in the aggregate and in the cement paste 2) the difference in concentration of mobile silicate ion in the aggregate and in the cement paste. Silicate ion was hypothesized as moving into, or out of, the aggregate depending on the relative concentrations of mobile silicate.

Reference is made, once again, to plate 1 which demonstrates the difficulty of obtaining a representative sample by such a method.

It was believed worth while to attempt to work out a procedure for better sampling of rocks, before and after shell
growth, and at the same time bring about shell growth in a reasonably short time, (i.e., short relative to three months). Once the above has been accomplished, many samples can be analyzed and even though a rock is quite inhomogeneous, trends will appear. Then one can, reasonably, either modify previous hypotheses or present new ones concerning shell growth.

Two possibilities presented themselves for shortening the length of time required for shell growth. A first possibility was demonstrated by Lemish (1959) who has shown that shells could be grown in a few hours at elevated temperatures and pressures. He used an autoclave procedure to obtain the desired conditions. A second possibility, and the one decided on here, was simply a reflux procedure.

B. Reflux Procedures

The experiments described in this section are only of the most preliminary type. However, they do result in a couple of interesting observations and they do point the way to some further experiments that might prove to be enlightening.

Since silicate ion, in solution, was to be determined, it was first necessary to determine the amount of silicate going into solution from the glassware of the reflux condensers. 500 ml. of distilled water was placed in the flasks and the pH adjusted to 12.0 by addition of NaOH solution. The water was set to boiling gently and allowed to reflux for 48 hours. At the end of that period, the weight of silicon in solution was
determined by use of a Beckman Model B spectrophotometer, according to the method of Banks and Carlson (1952). Several determinations were made on both soft glass apparatus and pyrex. The average value for total silicon in solution in 500 ml. H2O from pyrex was 73 miligrams; for soft glass it was 100 miligrams. See Table 1.

Banks and Carlson (1952) showed that treatment of silicon unknowns with hydrofluoric acid was essential to convert all the soluble silicon to a reactive form. It was suspected that the nonreactive form is comprised of some larger and more complex ion than monomeric silicate ion.

It was early thought (Bisque and Lemish 1958) that shell growth was a function of the disorder that existed in the structure of the clay particles in a carbonate rock. It is further reasoned that if various degrees of disorder exist among the clay particles, then the degree of disorder should manifest itself in the distribution of particles which that particular rock supplies for solution. Thus, it was decided to run two samples on each unknown; one with HF treatment, one without HF treatment. This would result in 1) total silicon and 2) molybdate reactive silicon. Thus, leading to the column, Table 1, titled "% reactive silicon".

It is interesting to note that, in the case of the glassware, the silicon was always 100% reactive.

In each of the following experiments 100 grams of material was chosen. The rock, or cement, was crushed and sieved. From
Table 1. Results of reflux experiments, silicon in solution

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Total mg. silicon in 500 ml. H₂O</th>
<th>% Reactive silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrex glass</td>
<td>73.0</td>
<td>100</td>
</tr>
<tr>
<td>Soft glass</td>
<td>100.0</td>
<td>100</td>
</tr>
<tr>
<td>Glory 2</td>
<td>65.0</td>
<td>97</td>
</tr>
<tr>
<td>Kenwood bed C</td>
<td>8.0</td>
<td>96</td>
</tr>
<tr>
<td>Mortar bar</td>
<td>1.0</td>
<td>86</td>
</tr>
<tr>
<td>Low alkali cement</td>
<td>0.9</td>
<td>88</td>
</tr>
<tr>
<td>Medium alkali cement</td>
<td>1.5</td>
<td>74</td>
</tr>
<tr>
<td>High alkali cement</td>
<td>1.3</td>
<td>54</td>
</tr>
<tr>
<td>Glory 2 in cement</td>
<td>1.0</td>
<td>50</td>
</tr>
<tr>
<td>Kenwood bed C in cement</td>
<td>1.2</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 2. Results of reflux experiments, gain in weight by a 25 gram specimen

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Gain in weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glory 2</td>
<td>0.033</td>
</tr>
<tr>
<td>Kenwood bed C</td>
<td>0.041</td>
</tr>
</tbody>
</table>
that portion passing the 0.263 sieve but remaining on the 0.131 sieve a sample was chosen. It was then washed with distilled water before refluxing. In choosing samples in this way, it is believed that a more representative specimen is obtained.

A one hundred gram sample of Glory 2, (a typical "poor" aggregate which has been observed to absorb silica and to grow reaction shells), was refluxed for 48 hours and silicon determined in solution. Total silicon in solution was found to be 65.0 mgs. Ninety-seven per cent of which was molybdate reactive.

At the end of the reflux period, a chip was taken from the boiling flask, broken open and leached in acid. A noticeable reaction shell was observed on the periphery of the chip. Also, the very thin bedding seams in the aggregate were observed to stand out in relief as if they were now more insoluble than had they been in the original rock. See Plate 2.

A one hundred gram sample of Kenwood quarry bed C, (an aggregate in which shell growth is postulated to occur by a mechanism other than absorption of silica), was refluxed for 48 hours and silicon, in solution, determined. Total silicon in solution was found to be 8.0 mgs. Ninety-six per cent of which was molybdate reactive.

One hundred gram samples of three standard cements, (obtained from the Portland Cement Association) were also refluxed. These standard cements contained 0.23% (low), 0.60% (medium) and 1.36% (high) alkali metal oxides. It was of interest to see
whether or not the amount of silicon supplied to the solution was a function of the amount of alkali metal present. Reference to Table 1 will show that a very small amount of soluble silicon was found over each of the cements. Low alkali cement had 0.9 mg.; 88% of which was molybdate reactive. Medium alkali cement had 1.5 mg.; 74% of which was molybdate reactive. High alkali cement had 1.3 mg.; 54% of which was molybdate reactive.

Concrete test specimens were poured using Soxhlet extractor thimbles as forms, (see Plate 3). This was done in an attempt to embed aggregate in concrete in such a manner that it could be quantitatively removed after refluxing. Table 1 shows, again, the low amount of silicon found in solution over the concrete. Table 2 shows that both the specimen from the Glory quarry and that from Kenwood bed C gained weight when placed in concrete in this manner and refluxed for 48 hours.

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

1. Introduction

Upon reviewing previous work (Bisque and Lemish, 1958, 1959), the author 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
Plate 3. Soxhlet extractor thimbles used for concrete forms.
decision to treat several specimens with a vaporous mixture of 
(CH₃)₂SiCl₂ and CH₃SiCl₃ and to examine the resultant rock.

2. Theory

Earlier investigators (Bisque and Lemish 1958, 1959) have shown that rocks, which contain a high percent of argillaceous material, absorb silica (from solution and from concrete paste) more readily than do pure carbonates. One might, then, reasonably postulate the occurrence of a condensation polymerization of the following type.

\[ \text{Clay Particle-OH} + n \text{Si(OH)}₄ = \text{Clay Particle-O-Si-O-Si-OH} + n\text{H}_₂\text{O}. \]

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 SiCl₂₄ (boiling point 57.6° C) to volatilize and to be hydrolyzed by the water vapor in the atmosphere (Rochow, 1951).

\[ \text{SiCl₂₄} + 4 \text{H}_₂\text{O} = \text{Si(OH)}₂₄ + 4 \text{HCl}. \]

The vaporous silicic acid thus formed would be available for polymerization with the argillaceous material contained throughout the rock. Since vaporous silicic acid possesses 4 reactive functional groups, one would anticipate 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).

\[(\text{CH}_3)_2\text{SiCl}_2 + 2\text{H}_2\text{O} = (\text{CH}_3)_2\text{Si(OH)}_2 + 2\text{HCl}\]

\[\text{CH}_3\text{SiCl}_3 + 3\text{H}_2\text{O} = \text{CH}_3\text{Si(OH)}_3 + 3\text{HCl}\]

Clay Particle-OH + (\text{CH}_3)_2\text{Si(OH)}_2 + \text{CH}_3\text{Si(OH)}_3 =

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

Clay Particle-o-Si-o-Si-o-Si---etc.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

(water repellent solid)

3. Experimental

The procedure and equipment used to impregnate the rock specimens with the various silanes is quite simple but effective. At the bottom of a glass dessicator is placed an evaporating dish containing 20 to 25 ml. of silicon tetrachloride or
20 to 25 ml. of an approximately equal volume mixture of di-
methyldichlorosilane and methyltrichlorosilane. The porcelain
dessicator plate is placed in position and the rock specimens
to be treated are positioned on top of that. A vacuum type lid
is placed on the dessicator with the vacuum vent open to atmos-
phere. The dessicator with its contents is then placed in a
hood and allowed to stand for several hours or for several days,
as desired. A reasonable amount of caution is suggested when
handling these materials since hydrochloric acid is a by-prod-
uct of the hydrolysis.

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

4. Results

Table 3 is presented in order to show the gain in weight
experienced by carbonate rocks placed in an atmosphere of sili-
con 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.

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

Specimens which had been treated with \(\text{SiCl}_4\) were found to
effervesce much more slowly when placed in \(\frac{1}{4}\) normal hydrochloric
acid than do untreated specimens. After one day's treatment, a
Table 3. Weight gained by rock specimens

<table>
<thead>
<tr>
<th>Time in days</th>
<th>Specimen number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>6.728</td>
</tr>
<tr>
<td>1</td>
<td>6.738</td>
</tr>
<tr>
<td>4</td>
<td>6.744</td>
</tr>
<tr>
<td>7</td>
<td>6.787</td>
</tr>
</tbody>
</table>

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.

Plate 4 shows a piece of untreated argillaceous limestone on the left and a similar piece of rock on the right which has been treated with dimethyldichlorosilane and methyltrichlorosilane. 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
Plate 4. Untreated carbonate specimen on the left. Treated specimen on the right. Note water repellency of treated specimen.

Plate 5. Untreated rock, left; treated rock, right; specimens placed in concentrated HCl.
the exterior surface only. After approximately four hour's treatment, rocks of about one inch diameter were broken open and were found to be water repellent throughout.

Plate 5 shows the result (left beaker) of placing a piece of argillaceous limestone in $\frac{1}{4}$ 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 $\frac{1}{4}$ normal HCl for two days when the picture was taken. In the case of the treated specimen, the carbonate was leached away very slowly leaving the insoluble argillaceous material in its original three-dimensional configuration.

Plate 6 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.

It is interesting to note (Table 3) 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.

Plate 7 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

Plate 7. Treated and untreated concrete. Note water repellency of treated specimen on the right.
contrasted to a non-treated specimen which readily effervesced and disintegrated. The final results of that acid leaching were similar to those of limestone specimens illustrated in Plate 5.

Following are some applications.

1. Beneficiation of limestones which fail to pass certain standard tests required of concrete aggregate.
2. Retardation of silicification of carbonate aggregates in concrete.
3. Retardation of the alkali-aggregate reaction.
4. Rendering concretes, cements and mortars water repellent as well as inert to acid solutions or to the effects of atmospheric carbon dioxide.
5. Improvement of the bond between carbonate aggregate and bituminous material in the construction of asphalt highways.
6. Improvement of cement blocks, bricks, and concrete structural members. That is, rendering them water repellent, less subject to disintegration due to freezing and thawing, and inert to weathering.
7. Improvement of crushed limestones used for the surfacing of highways, driveways, or parking lots. That is, rendering them less susceptible to freeze-thaw losses and the elimination of pumping due to capillary action.
8. Improvement of rolled stone base on which concrete highways are to be laid. That is, the reduction of
freeze-thaw losses and the elimination of the undesirable pumping action.

Consideration of the above practical applications of silane treated aggregate and concrete materials, naturally, suggested the advisability of applying for patent on the process. See the appendix for copy of original application and first amendments.
V. DETERMINATION OF RELATIVE ABUNDANCE
OF CALCITE AND DOLOMITE IN CARBONATE ROCKS

A. Procedure

The problem of determining the relative proportions of calcite and dolomite in a rock arises naturally when one considers a carbonate rock's suitability for use as concrete aggregate. This is a problem which has, also, long concerned the sedimentary petrologist.

Calcite and dolomite are quite similar optically and at best only a fair approximation can be obtained by a thin-section traverse, even though careful etching and counting procedures are employed (Belyankin, et al., 1940). Furthermore the two minerals are quite similar in their chemical properties and, thus, it has remained, to date, impossible to quantitatively separate them. Slight differences in their rates of solution in acid media have been reported, however (Weyl, 1957, 1958). That difference is the basis upon which staining procedures have been formulated, which purport to give estimates of calcite-dolomite ratios in carbonate rocks (Weissmann and Diehl, 1953, Lawson, 1950).

Staining procedures take advantage of the fact that calcite goes into solution at a slightly faster rate than does dolomite and will impart a characteristic color to a prepared dyestuff more quickly than will an equivalent amount of dolomite. Obviously, in such a procedure, sample preparation will be critical. Rate of solution of both calcite and dolomite is
surely a function of surface area exposed to solvent and, therefore, particle size is a critical factor.

Another variable upon which rate of solution, of both calcite and dolomite, will surely depend is composition. That is, the amount of excess calcium, or magnesium, above the ideal one to one ratio in dolomite; or the amount of magnesium ion in solid solution in calcite. These are factors which have, as yet, not been investigated and their influence on staining techniques have not been evaluated. It is believed that answers to such problems are forthcoming, however, as is evidenced by the careful work of Weyl (1957, 1958) on the solution kinetics of calcite.

Tennant and Berger (1957) proposed an x-ray method which, according to those authors, has the advantage of giving results proportional to the total amount of material present having the calcite and dolomite structure types. Those authors state that a correction would be necessary in the x-ray calibration if a sample showed a variation from the ideal calcite (CaCO$_3$) or dolomite (CaMg(CO$_3$)$_2$) composition. Their method consists of measuring the relative intensities of the strongest x-ray diffraction line for calcite and for dolomite in a series of mixtures of known proportions, and applying those results to samples of unknown composition. That series of mixtures of known compositions gave rise to the smooth calibration curve illustrated in Figure 3.

Those authors found, when attempting to reproduce points
Figure 3. X-ray intensity ratio as a function of % dolomite.

Figure 4. Variation of Co for the Ca-Mg carbonates.
CALIBRATION CURVE

% DOLOMITIZATION OF CALCITE

X-RAY INTENSITY RATIO

Mol PERCENT MgCO₃ in CaCO₃
on the calibration curve, that preparation of sample was most critical. The samples were reduced to -325 mesh and subsequently wet ballmilled for 15 hours in the presence of ethyl alcohol. Tests showed that a grinding period of at least eight hours is essential.

Hiltrop (1958) attempted to delineate those characteristics of a carbonate rock which determine whether or not it will satisfactorily serve as aggregate for concrete highway construction. He presented a method, based on conditional probabilities which indicated that high illitic clay content and low calcium to magnesium ratio (high dolomite content) correlated well with "poor" service record.

More recently, other investigators have called on a dedolomitization reaction (Swenson and Gillott, 1960, Feldman and Sereda, 1960, Hadley, 1960, Chaiken and Halstead, 1960) in an attempt to explain the deteriorous role played by some carbonate aggregates in concrete. Dedolomitization is depicted as involving the following reaction.

\[
\text{Ca}_{1-y}\text{Mg}_y\text{CO}_3 + 2z\text{OH}^- = \text{Ca}_{1-y}\text{Mg}_{y-z}\text{CO}_3 \text{ I-} - z + z\text{Mg(OH)}_2 + z\text{CO}_3^- \\
\text{Dolomite base Dolomite Brucite Carbonate I II}
\]

Dedolomitization, according to the above authors, is accompanied by weakening of the aggregate and/or of the cement paste.

Reports such as that of Hiltrop (1958) and of Swenson and Gillott (1960) lead one, once again, to consider the problem of
determining calcite-dolomite ratio in a carbonate rock.

A method is proposed, here, which employs a combination of wet chemistry and x-ray techniques. Final results are obtained by the solution of a pair of simultaneous equations.

Consider a hypothetical carbonate rock which is composed of the two minerals calcite and dolomite. Assume that the average composition of the calcite is $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$, and the average composition of the dolomite is $\text{Ca}_{1-y}\text{Mg}_y\text{CO}_3$. The value of $x$ will lie on the closed interval where $0 \leq x \leq 0.22$ and $y$ will lie on the closed interval where $0.44 \leq y \leq 0.51$.

Graf and Goldsmith (1955) investigated the dolomite-magnesian calcite relations at elevated temperatures and pressures. They obtained equilibrium diagrams for those minerals. Their curves show that calcites and dolomites whose compositions vary from the ideal are unstable at normal atmospheric temperatures and pressures. Other investigators have reported the existence of such metastable phases, in nature, however.

Goldsmith, Graf and Joensuu (1955) have demonstrated the existence of calcites in which the mole percent $\text{Mg}^{++}$ in solid solution in the calcite can be as high as 20.8%. Alderman (1959) has found dolomitic sediments being deposited in shallow oceanic lagoons. The deposits contain magnesian calcites which have up to 22% $\text{MgCO}_3$ in solid solution. Also calcian dolomites are present, in the sediments, having up to 6% excess $\text{Ca}^{++}$ ion. Goldsmith (1959) has formed synthetic dolomites which have about one percent excess $\text{Mg}^{++}$ ion above the ideal 1:1 ratio.
Thus, even though such solid solutions are unstable, it is apparent that they do exist and, furthermore, our choice of values for x and y seems reasonable in the light of present knowledge.

It is apparent that if one were to simply dissolve our hypothetical carbonate rock and analyze for Ca$^{++}$ and Mg$^{++}$ in solution, he could possibly arrive at quite erroneous results by assigning the composition, CaCO$_3$, to calcite and, CaMg(CO$_3$)$_2$, to dolomite. That is the procedure which has been followed in the past and is the difficulty which this proposed method hopes to circumvent.

Consider, once again, a small chip of hypothetical rock which is composed of $N_c$ moles of calcite and $N_d$ moles of dolomite having the compositions $Ca_{1-x}Mg_xCO_3$ and $Ca_{1-y}Mg_yCO_3$ respectively. The problem is to experimentally determine $x$, $y$, $N_c$ and $N_d$.

Since it is generally agreed that calcite dissolves more rapidly than does dolomite, it seems that it would be possible to collect pure dolomite by leaching away all the calcite. Such a possibility seems even more promising in the case of those rocks which are composed of relatively coarse dolomite rhombs distributed throughout a matrix composed of very fine calcite grains. Such a leaching procedure was accomplished and x-ray diffraction curves, of the dolomite concentrate, indicate the absence of calcite.

The method used to collect the dolomite fraction is as
follows. About 50 grams of rock is pulverized to \(-\frac{1}{8}\) inch and placed in a beaker of 30% acetic acid. Leaching is allowed to continue for several days and then the undissolved portion is washed through a series of sieves. In the case of the two rocks examined here, that fraction passing the number 270 sieve but remaining on the number 325 was found to give no X-ray diffraction peaks indicative of the presence of calcite. In such a leaching procedure, one assumes that all the calcite has been removed as well as some of the dolomite. Pure dolomite has been collected but a quantitative separation has not been accomplished. This results in the necessity of solving a set of simultaneous equations.

Once pure dolomite has been collected, the calcium to magnesium ratio in the mineral can be determined by titration with versenate as described by Cheng et al. (1952). The results of these determinations are presented in Table 4.

With the publication of data which show the relationship between carbonate lattice constants and calcium-magnesium composition (Goldsmith and Graf, 1958) an alternative method for determining calcium to magnesium composition in dolomite has become available. A comparison of the results of these two methods is also presented in Table 4.

Goldsmith and Graf hypothesized that lattice spacings in calcite should be a linear function of the amount of magnesium in solid solution. The upper line in Figure 4 is a straight line connecting \(c_0\) \((d_{10\overline{1}2})\) for calcite with \(c_0\) for magnesite.
Table 4. Experimental results, calcite-dolomite ratios

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Burlington limestone</th>
<th>RL - 40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical dtrm. dolomite</td>
<td>Ca$<em>{56}$Mg$</em>{44}$CO$_3$</td>
<td>Ca$<em>{54}$Mg$</em>{46}$CO$_3$</td>
</tr>
<tr>
<td>2θ Dolomite 10T12</td>
<td>70.15°</td>
<td>70.50°</td>
</tr>
<tr>
<td>2θ Calcite 10T12</td>
<td>65.77°</td>
<td>65.60°</td>
</tr>
<tr>
<td>Co</td>
<td>16.0848</td>
<td>16.0152</td>
</tr>
<tr>
<td>Dolomite Co</td>
<td>17.0332</td>
<td>17.0628</td>
</tr>
<tr>
<td>Calcite</td>
<td>X-ray dtrm. dolomite</td>
<td>Ca$<em>{54}$Mg$</em>{46}$CO$_3$</td>
</tr>
<tr>
<td>X-ray dtrm. calcite</td>
<td>Ca$<em>{99}$Mg$</em>{01}$CO$_3$</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>Ca$^{++}$</td>
<td>0.0079</td>
<td>0.0091</td>
</tr>
<tr>
<td>Mg$^{++}$</td>
<td>0.0058</td>
<td>0.0052</td>
</tr>
<tr>
<td>Mole % calcite based on chem. dtrm. of dolomite</td>
<td>3.7%</td>
<td>21.0%</td>
</tr>
<tr>
<td>Mole % calcite based on x-ray dtrm. of dolomite</td>
<td>8.0%</td>
<td>25.9%</td>
</tr>
</tbody>
</table>
Small circles indicate experimentally determined points. It can be seen that the four calcites examined by Goldsmith and Graf determine a straight line which lies slightly below the first line. This lower line was employed to determine the amount of magnesium in solid solution in calcite. Goldsmith and Graf also examined four dolomites and found their compositions and lattice spacings to plot as indicated by the three small circles on the graf. (Two of the experimental points coincide). If a straight line is drawn through these three points and extended to the value for pure calcite, one has a means of experimentally estimating the calcium to magnesium ratio in a dolomite. A segment of such a line is shown in Figure 4. By making use of this straight line and x-ray determined \( C_0 \) spacings, one has an alternative method for estimating the composition of dolomite. That is, there are two independent methods to estimate \( y \) in the original problem.

Now, once again, take a chip of the original rock and completely dissolve it in hydrochloric acid. The number of moles of calcium ion and magnesium ion in solution, can be determined by the versenate method. Once that is done, one can set down the following pair of simultaneous equations.

\[
\begin{align*}
\text{Ca}^{++} &= (1-x)N_c + (1-y)N_d \\
\text{Mg}^{++} &= xN_c + yN_d
\end{align*}
\]

(1)

(2)

where \( y \) has been determined by either of the methods discussed above. Equations (1) and (2) form a pair of independent
simultaneous equations in three unknowns. In order to solve for the unknowns, there must be either another independent equation supplied or one of the unknowns must be determined by independent means. The latter method is employed here. The variable quantity $x$ is obtained by determining $C_0$ spacings and referring to Goldsmith and Graf's straight line function (Figure 4). When that has been done, equations (1) and (2) reduce to a pair of simultaneous equations in two unknowns and can be solved for $N_c$ and $N_d$. This, then, is equivalent to determining the molar ratio of calcite to dolomite in the original rock.

B. Experimental Results

The mole percent calcite, relative to total carbonate present, was determined in two rocks. Those two rocks are designated as 1- Burlington limestone and 2- RL-40. Pertinent data concerning that determination, as well as the final results, are presented in Table 4.
VI. pH INVESTIGATIONS OF AGGREGATE AND CEMENT

One of the basic postulates in Harwood's (1960) hypothesis of shell growth was that in hardened concrete the pH was higher in the cement than on the interior of the aggregate. Such a premise seems reasonable since limestone in water equilibrates at a pH of about 9, while cement in water equilibrates at about 12. In order to get a better idea of the pH conditions in hardened concrete, the block pictured in Plate 8 was prepared. A cube of Kenwood bed C, 2" x 3 1/2" x 3", was set into cement as pictured. Several small holes were formed in the cement, and several were drilled in the limestone. The holes were stoppered with corks, and rubber stoppers, and the whole concrete block placed in distilled water to a depth level with the top of the cement paste.

It was believed that the cement and the limestone cube would become saturated after a few days and one could sample the solution in the holes and determine pH. Such was not the case. Some water did manage to find its way into the holes in the cement but the limestone was dry even after two weeks. It was then decided to fill the ports with distilled water and check the pH periodically. By use of pH paper, equilibrium OH\textsuperscript{-} ion concentration was found to be about 9 in the rock and about 12 in the cement.
Plate 8. Limestone aggregate set in concrete in order to investigate pH.
VII. DISCUSSION

Rock materials, mortar, and concrete materials treated with the vaporous organosilanes might be used to advantage in many situations. In any situation where additional strength, or water repellency, or greater resistance to weathering, or to freezing and thawing is a desirable characteristic, such treatment might be useful. The treatment might also be useful in any situation where the material would be subjected to the leaching action of either acidic or basic solutions. This treatment is particularly effective because the vaporous, molecular organosilane quickly and thoroughly permeates the material. The protective coat, thus applied, is not only on the exterior surface of the rock (or mortar, or concrete), but is distributed completely throughout the matrix as well.

The fact that the carbonate can be completely leached away from an argillaceous limestone (refer again to Plate 5) which has been treated in the organosilane, leaving the insoluble residue with all its original bedding, its structure, its texture, and other three-dimensional 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 author feels that 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.

It is not claimed that the above procedure for determining calcite-dolomite ratios is the "last word" on the subject. Not at all. What is claimed is that this is an alternative method for such a determination. Several specimens should be examined for calcite/dolomite by this method and by the method of Tennant and Berger (1957) and the results compared. Furthermore, this method claims to give only average values for $x$ and $y$. In some rocks, at least, it would seem probable that the composition of both the calcite and the dolomite would vary from place to place within the rock. Tennant and Berger are aware of this fact and admit that the effect of such a variation on intensity of x-ray reflection has not been investigated.

Another simplification which has been made, in order to outline the method as briefly and straightforwardly as possible, is to consider dolomite to be composed of only calcium and magnesium. It is known that it may contain a significant proportion of iron and manganese as well. This is a factor which other workers may wish to take into consideration. It is possible that such a consideration may lead to a third independent equation which, in turn, will allow the evaluation of $x$, $N_c$ and $N_d$. For example, if it is found that the dolomite, once having been collected, has the formula $Ca_{1-y}Mg_yFe_wCO_3$ and if it can be shown that all the iron which goes into solution is from the dolomite, then a third independent equation has become available. That is, the number of moles of iron in solution, $Fe^{++}$,
is equal to the number of moles of dolomite, \(N_d\), which went into solution, multiplied by \(w\).

\[
Fe^{++}_S = wN_d .
\]  

(3)

Another interesting avenue of research is made apparent when one considers equations (1) and (2). Addition of equations (1) and (2) gives

\[
Ca^{++} + Mg^{++} = N_c + N_d .
\]  

(4)

Now, if the assumption is made that the method of Tennant and Berger gives reliable information concerning the calcite to dolomite ratio in a rock, a new method becomes available for determination of \(x\) and \(y\). For if a value for \(\frac{N_d}{N_d + N_c}\) is obtained, (as it is in the Tennant and Berger method), that is equivalent to adding a third independent equation to our original pair of simultaneous equations, (i.e., equations 1 and 2).

For example, if

\[
\frac{N_d}{N_d + N_c} = K ,
\]

then

\[
N_d = \frac{KN_c}{1 - K} .
\]  

(5)

Substitution of this quantity for \(N_d\) in (4) allows the evaluation of \(N_d\) and \(N_c\). Then equations (1) and (2) can be solved for \(x\) and \(y\).
Results obtained in that way could be compared with those obtained by Goldsmith and Graf's x-ray method.

Another interesting approach to the evaluation of $\mathrm{c}$ is afforded by the work of Harker and Tuttle (1955). They showed that the weight per cent $\mathrm{MgCO}_3$ in solid solution in calcite is a straight line function of the change in position of the 29.3° 2$\theta$ x-ray diffraction peak of calcite. In order to accurately measure the change in 2$\theta$ a convenient standard was added to the unknown. The material which was chosen for a standard was cadmium fluoride. That standard was found to have its strongest peak at an angle of 0.72° 2$\theta$ below that of pure calcite. Using such a standard peak for reference, it was possible to measure the angular shift in the position of the strongest peak of calcite with an accuracy of $\pm$ 0.01°.

The first basic premise in Harker's (1960) hypothesis was that $\mathrm{OH}^-$ ion concentration is lower in the aggregate than in the cement paste. Evidence presented here supports that premise (again see Plate 8).

The second basic premise was that silicate ion would migrate into or out of an aggregate depending on the relative amount of silicate ion available for solution in the aggregate and in the cement paste. It was reasoned that silicate ion would migrate away from the area of high concentration and into the area of low concentration. Evidence presented here (Table 1) indicates that soluble silicate is always very low in the hardened cement paste. Furthermore, Glory 2 (an aggregate
which was agreed to grow a reaction shell by adsorption of silica) appears to supply a greater amount of silicate for solution, (by a factor of about 8), than does Kenwood bed C, (an aggregate which was postulated to decrease its silicate content in the process of growing a reaction shell). Also, (refer to Table 2), both Glory 2 and Kenwood bed C specimens gained weight when refluxed in the cement paste environment. If Glory 2 grows a shell by absorption of silica, one would expect it to gain weight, as it does. However, if Kenwood bed C grows a shell by net loss of silica, one would expect it to lose weight.

Such evidence and hypotheses appear to be at variance with one another.

It is interesting to point out that the boiling flasks which contained Glory 2, Kenwood bed C and all the cement specimens, were each lower in soluble silicate than were the flasks which contained only water adjusted to pH 12. Furthermore, the fact that some of the solutions contained appreciable percentages of nonreactive silicate ion, lends some support to the earlier hypothesized distribution of silicate polymer chains in solution.

Both Bisque and Lemish (1958) and Harwood (1960) believed that shell growth was a function of the presence of certain reactive sites of deposition in inferior aggregate. Bisque believed those reaction sites were Si-OH groups at the edges of, (or wherever broken -Si-O-Si- bonds might occur in), the clay particles (illites) present.
An interesting phenomenon was observed that might have some bearing on that point. In each run where hardened cement was being refluxed, the boiling flask itself became coated with a thick white solid which clung tenaciously to the inside of the flask. Obviously the glassware is a source of silicate ion. The glassware provides an environment high in molybdate reactive silicate. Evidently the cement is supplying some component which fixes that silicate ion almost as soon as it is made available for solution. Just possibly that component is \( \text{Ca}^{++} \) ion, or \( \text{AlO}_2^- \) ion, or both. Perhaps a similar mechanism is taking place in the inferior aggregate.

The question remains - what conditions determine which direction silicon moves? The fact that the Kenwood bed C rock absorbs more silicate from solution than does Glory 2 might possibly be explained on the basis that Kenwood bed C possesses more active sites for condensation than does Glory 2.

What is needed is 1) a method for selecting representative samples. 2) A method for growing shells in a relatively short time, under a variety of conditions, and especially in silica free containers. Perhaps some adaptation of the reflux methods, perhaps some adaptation of the Soxhlet extractor thimble procedure will prove useful.
VIII. SUGGESTIONS FOR FUTURE WORK

Critical questions at this point in the program are still, under what conditions does silicon move into the shell zone? Under what conditions does silicon move out of the shell zone?

Such questions can be determined by selecting a sizeable sample of several different aggregates, treat them in such a manner as to have as nearly representative samples as possible, then analyze several specimens from each sample before and after shell growth. The mean values obtained in this way would be invaluable in attempting to postulate a mechanism for shell growth. Obviously, to speak of mechanism of reaction is meaningless unless one can first be certain of what are reactants and what are products.

Refluxing experiments should be carried on in plasticware, rather than in glass ware. After refluxing, molybdate reactive silicon, as well as total silicon, could be determined colorimetrically. Possibly one of these values might correlate with a rock's susceptibility to silicification.

Another interesting approach would be through the use of vaporous \((\text{CH}_3)_3\text{SiCl}\). This compound has only one chlorine for hydrolysis and, thus, cannot lead to polymer formation. One could subject a rock to vaporous \((\text{CH}_3)_3\text{SiCl}\); weigh before and after treatment. Such a procedure would amount to "counting" available reactive functional groups in the specimen. Perhaps the value obtained in this manner would correlate with
susceptibility to silicification.

The method, proposed above, for determination of calcite-dolomite ratios should be valuable in testing the validity of the dedolomitization theory. Calcite-dolomite ratios could be determined, in a series of rocks, before and after shell growth.

From the recent arguments put forth by the proponents of a deleterious "dedolomitization" reaction, calcite-dolomite ratios as well as calcite and dolomite compositions would appear more critical than simply total Ca$^{++}$ ion and Mg$^{++}$ ion composition.

An attempt could be made to bring about dedolomitization of a rock in the laboratory. The quantities $x$, $y$ and $\frac{N_d}{N_c + N_d}$ should be determined as accurately as possible before and after dedolomitization has taken place. Investigations in this direction may lead to a better understanding of the reaction, its extent, its rate and degree to which it is harmful to concrete.

Very preliminary experiments have shown the feasibility of preparing very thin sections of rock which have been treated with a mixture of CH$_3$ SiCl$_3$ and (CH$_3$)$_2$SiCl$_2$. After treatment with the vaporous organosilanes, the rock is leached with HCl and set into melted paraffin and allowed to cool. By use of a microtome, thin sections as thin as one micron have been prepared. Electron micrographs of such thin sections, may contribute to an understanding of the shape and arrangement of clay particles as they occur naturally in a carbonate rock.
Additional studies of pH in aggregate and cement paste should be made. Smaller blocks of aggregate could be used and lesser thicknesses of cement placed around the aggregate. In this way, water may more easily and more quickly saturate the concrete. Also very small holes could be drilled, by use of a dentist's drill, near the aggregate-cement paste interface. In this way, a better idea might be obtained as to the constitution of the water solutions in the zone which ultimately becomes the reaction "shell" zone.
IX. LITERATURE CITED


Richardson, E. and Waddams, J.A. 1954. Use of the silico-molybdate reaction to investigate the polymerization of low molecular weight silicic acids in dilute solutions. Research Correspondence, Supplement to 7: No. 7, 542-543.


X. ACKNOWLEDGEMENTS

The author wishes to express a sincere thanks to Dr. C.J. Roy, Head of the Department of geology at Iowa State for the presence and availability of the very capably staffed geology department; and thanks for granting permission to conduct this research in his laboratories.

A special debt of gratitude is owed Dr. John Lemish, who was the immediate supervisor on this project, for his encouragement and ever present enthusiasm.

A word of appreciation to Mike Werner, Bob Harwood and Frank Diebold, fellow graduate students with whom I shared the laboratory, for their patience and cooperation.

Thanks to Nick Saum for enthusiastically performing many time consuming tasks.

A debt is owed the Iowa State Highway Commission who financed this project.

And lastly, a very, very special thanks to Francie, my wife. She has uncomplainingly, (actually happily), worked full time all these years in order to keep the wolf away from the door. She has kept the home spotless and our clothing pressed and clean. She has prepared the meals and done the other thousand and one necessary tasks about a home. And through all of this, she has been the one steady, guiding light. She absolutely refused to allow us to quit even when things appeared blackest. All thanks to Francie.
XI. APPENDIX: HILTROP AND LEMISH APPLICATION FOR PATENT

A. Original Application

1. Aggregate treatment

This invention relates to aggregate treatment and, more particularly, to the treatment of rocks useful as aggregate in concrete wherein the physical properties of the aggregate are improved and which is productive of a concrete having improved resistance to failure.

The aggregate portion of concrete which may constitute 80% or so of the concrete often includes argillaceous carbonate and dolomitic rocks. We have noted that such rocks develop a shell at their surfaces when incorporated in concrete. The development of these shells is attended by a general weakening of the concrete itself so that there is an increased possibility of failure. Highway sections which had proven unsatisfactory in service were noted to possess these shells on the periphery of the carbonate aggregate. The shell portions we have termed "reaction shell" and it has been conclusively demonstrated that these reaction shells are richer in silica than was the original host rock. Thus it seems 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". Highway sections wherein the aggregate shells were lacking have proved uniformly stronger and more resistant to failure. For the most part, the rocks lacking
the reaction shells can be characterized as lacking argil-
laceous components, i.e., illitic clays.

It is a general object of this invention to provide a
method of treating rocks, such as are useful in providing the
aggregate portion of concrete and especially argillaceous lime-
stone and dolomites whereby the physical properties of such
rocks are materially improved. The invention also contemplates
improving the argillaceous rocks to an extent that they func-
tion as well, if not better than the rocks lacking reaction
shells when employed as the aggregate in concrete.

Another object of the invention is to provide a novel
method of treating rocks through the contacting thereof with a
silicon containing gas, such as a silicon halide or an organo-
siliconhalide, whereby a small quantity of the silicon-contain-
ing material is dispersed throughout the rock and renders the
rock exceptionally strong for use as an aggregate in concrete.
Concrete utilizing such treated materials manifests exceptional
resistance to the failure ordinarily developed by the concrete
being subjected to a number of freeze-thaw cycles and other
stresses which would have a deleterious effect on concrete
utilizing non-treated rock aggregate.

Still another object is to provide a method of treating
rocks with an organosiliconhalide gas, such as a methylchloro-
silane, whereby the rocks are generally beneficiated, especially
when used in constructions subject to stress. Other objects
and advantages of this invention can be seen as this
specification proceeds.

In one aspect of the invention, we impregnate rock specimens with a gaseous derivative of silane. Preferably, the silane is a silicon halide with the halide moiety being bromine or chlorine. Of these, chlorine is preferred inasmuch as these silicon halides are generally inexpensive. Only a very small quantity of the silane is required for the impregnation, and it is believed that the mechanism of impregnation is attended by a molecular dispersion of the silane with the rock matrix. The silane, thus, may be silicon tetrachloride, an organic substituted chlorosilane such as dimethyldichlorosilane, methyltrichlorosilane, monomethyldichlorosilane, etc. With rocks of a size suitable for aggregate, we have found that the contact of the rock with the gaseous silane should be for a time of from a few hours to about four days under ordinary atmospheric conditions to develop satisfactory impregnation.

Illustrative of the invention is the following example.

2. Example 1

Two glass desiccators were provided, each having supported therein an evaporating dish. In one evaporating dish, 25 milliliters of silicon tetrachloride was placed. In the other evaporating dish 25 milliliters of an approximately equal volume mixture of dimethyldichlorosilane and methyltrichlorosilane was placed. The desiccators were equipped with porcelain desiccator plates and 1" carbonate rock chip specimens were placed on the
plate of each desiccator. The carbonate rock specimens for each desiccator were substantially identical, being of the same size, quantity, and possessing the same type and amount of clay impurity. A vacuum-type lid was placed on each desiccator with the vacuum vent left open to the atmosphere. Each desiccator with its contents was then placed in a hood. This precaution was taken since hydrochloric acid was generated as a byproduct of the hydrolysis. The silicon-containing materials were technical grade reagents provided by the Dow Chemical Company of Midland, Michigan. After one day's treatment, the rocks exposed to vaporous silicon tetrachloride were observed to possess a very noticeable insoluble reaction shell. Those rocks in the second desiccator, after having been exposed to the vaporous dimethyldichlorosilane and methyltrichlorosilane for approximately four hours, were observed to be completely water repellent throughout.

Another investigation was undertaken to determine the effect on rocks of different degrees of purity insofar as clay content was concerned. The procedure and results are set forth in Example 2 below.

3. Example 2

Three desiccators were provided with the evaporating dishes and plates enclosed, and with a vented vacuum-type lid. Each of the three desiccators contained an evaporating dish holding 25 milliliters of silicon tetrachloride. Three specimens were
provided, each consisting of rock chips approximately one inch in diameter, the chips being oven-dried overnight before the treatment was begun. The chips were also oven-dried each time before weighing. The specimen designated No. 1 contained the least clay (i.e., was the purest carbonate), while the specimen designated No. 3 contained the most clay. As can be seen from the table below, the specimen No. 1 which was the purest carbonate also showed the least gain in weight.

Table 5. Weight gained by rock specimens

<table>
<thead>
<tr>
<th>Time in days</th>
<th>Specimen number</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>0</td>
<td>6.728</td>
</tr>
<tr>
<td>1</td>
<td>6.738</td>
</tr>
<tr>
<td>4</td>
<td>6.744</td>
</tr>
<tr>
<td>7</td>
<td>6.787</td>
</tr>
</tbody>
</table>

Based on original weight, specimen number 1 showed an increase of 0.88%; specimen number 2, 1.36%; and specimen number 3, 1.75%.

In this example, the chips were placed in an atmosphere of dimethyldichlorosilane and methyltrichlorosilane between the fourth and seventh days. Thus, it appears that the organic silanes are somewhat superior in impregnating the rock specimens.
than the silicon tetrachlorides.

Specimens which have been treated with silicon tetrachloride were found to effervesce much more slowly than the untreated specimens when placed in $\text{H}_2\text{N}_2\text{H}_4$ hydrochloric acid. However, the pure carbonates remained noticeably more soluble in hydrochloric acid after treatment while the more inferior (i.e., more argillaceous) rocks evidenced considerably less reactivity with hydrochloric acid.

Comparing treated and untreated argillaceous limestone relative to water repellency demonstrates that the treated rocks are considerably more water repellent. It is significant to note that the water repellency effect is not limited to the exterior surface of the rocks only. After approximately four hours treatment, rocks of about 1" diameter were broken open and were found to be water repellent throughout. The water-surface contact angle in such rocks is estimated to be about $110^\circ$.

When treated rocks were subjected to degradation with a four normal ($4\text{N}$) hydrochloric acid, the carbonate was leached away very slowly leaving the insoluble argillaceous material in its original three-dimensional configuration. In contrast to this, an untreated similar specimen was completely broken down to sediment.

It is believed that the invention can be used to advantage in many situations, such as where rock materials, mortar, and concrete material are employed. This is particularly true in
those situations where additional strength, water repellency, and greater resistance to weathering or to freezing and thawing is desirable. The treatment is useful in those situations where the material would be subjected to the leaching action of either an acid or basic solution. For example, it has been observed by the inventors that treatment with vaporous organosiliconhalides, as described above, renders hardened concrete products water repellent as well as much less subject to degradation and/or leaching by either normal or basic or acidic waters. It is believed that this treatment is particularly effective because the vaporous, molecular organosilane quickly and thoroughly permeates the material. The protective coat, thus supplied, is not only on the exterior surface of the rock, but is distributed completely throughout the matrix as well.

While in the foregoing specification we have set forth a detailed description of an embodiment of the invention, it will be apparent to those skilled in the art that many modifications in the details herein given may be made without departing from the spirit and the scope of the invention.

4. Claims

We claim:

1. In a method of improving the resistance of concrete to failure, the step of contacting rock aggregate with a silicon-containing gas.

2. The method of claim 1 in which the said gas is a silicon
3. The method of claim 1 in which the said gas is a methylchlorosilane or other organohalosilane.

4. The method of claim 1 in which the said contact occurs for a time sufficient to permeate the rock aggregate with said gas.

5. The method of stabilizing concrete against stress failure comprising contacting argillaceous rocks with a silicon halide or an organosiliconhalide, and thereafter blending said rocks with cement to form concrete.

6. The method of claim 5 in which said silicon derivative is a gas.

7. The method of claim 6 in which the step of contacting occurs for a period of from a few minutes to several days.

8. In a method of improving the physical characteristics of rocks suitable for aggregate, the step of contacting said rocks with a silicon halide or an organosiliconhalide.

9. In a method of strengthening argillaceous rocks adapted for use as an aggregate in concrete, the step of contacting said rocks with a silicon halide gas or an organosiliconhalide gas.

10. In a method of rendering hardened concrete less susceptible to degradation and/or leaching, the step of contacting said concrete with a silicon halide gas or an
organosiliconhalide gas.

11. In a method of improving the asphalt to aggregate bond, the step of contacting said aggregate to a silicon halide gas or an organosilicon halide gas.
B. Notification of Official Action

1. Letter from attorney

DAWSON, TILTON, FALLON & LUNGMUS
Attorneys at Law
209 South La Salle Street
Chicago 4, Illinois

December 10, 1959

Mr. Quincy C. Ayres
Iowa State College Research Foundation, Inc.
108 Morrill Hall
Ames, Iowa

Re: Hiltrop and Lemish Application
Serial No. 828,682

Dear Quincy:

We recently received an official action in the above identified case and more recently have received the five references cited against the application.

A copy of the Official action is enclosed for your files and the references are also enclosed which we should like returned with any comments the inventors might have on their pertinency. A good part of the Official action is concerned with formal matters - the form of the claims which we can argue successfully, we believe. The Examiners are always wanting applicants to put down specific conditions, i.e., time, temperature, etc. and we only go to this where it will not unduly limit the invention. The more immediate problem is to determine just how much we should circumscribe our definition of invention because of the references. Inasmuch as Dr. Lemish grasps the problems of patent prosecution rather well, we thought it desirable to have his comments on the case before we did anything insofar as amending it.

We have until March 28 in which to file our reply and would like to have any comments and the references returned say about a month before that time.

Best personal regards.

Very truly yours,

DAWSON, TILTON, FALLON & LUNGMUS
2. Communication from examiner

DEPARTMENT OF COMMERCE
United States Patent Office
Washington

Carl L. Hiltrop et al.
Ser. No. 828,682
July 22, 1959
AGGREGATE TREATMENT

This application has been examined.

References applied:

<table>
<thead>
<tr>
<th>Reference</th>
<th>Patent No.</th>
<th>Date</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safford I</td>
<td>2,510,661</td>
<td>June 6, 1950</td>
<td>106-287 C</td>
</tr>
<tr>
<td>Safford II</td>
<td>2,563,555</td>
<td>Aug. 7, 1951</td>
<td>106-308 I</td>
</tr>
<tr>
<td>McLaughlin</td>
<td>2,676,892</td>
<td>Apr. 27, 1954</td>
<td>106-97</td>
</tr>
<tr>
<td>Wagner</td>
<td>2,795,206</td>
<td>Mar. 29, 1955</td>
<td>106-287 A</td>
</tr>
<tr>
<td>Sommer</td>
<td>2,706,688</td>
<td>Apr. 19, 1955</td>
<td>106-287 A</td>
</tr>
</tbody>
</table>

All the claims are rejected as not particularly pointing out and distinctly claiming the invention as required by Rule 75(a). The claims are incomplete; note claim 1 drawn to a method of improving concrete resistance to failure, but only one step in the method is set forth, also claim 5 drawn to stabilizing concrete and only the step of "contacting" and "blending" are set forth. The claims are functional in claiming results such as "contacting", "permeate", and "blending", without stipulating the operating conditions such as time, temperature, pressure, etc. The claims are indefinite in not giving the reactants and their proportions. The terms "rock aggregate", "argillaceous rocks", "rock", and "aggregate" are too broad and indefinite; applicant has support for "carbonate rock chip specimens" containing clay impurity. The terms "a silicon-containing gas" "a silicon halide", "a methylchlorosilane", 

and "an organosiliconhalide gas" are too broad and indefinite. The term "cement" is too broad. Claim 5 is inoperative if one were "to blend" silicon halide treated argillaceous rock with "cement" one would not obtain concrete. The term "a time sufficient to permeate" is too broad and indefinite. The terms "few" and "several" are too broad and indefinite. Applicant makes the statement as to time on page 3 "a few minutes to about 4 days"; on page 4, 1-day treatment, and 4-hours treatment; and on page 6, 4th and 7th days.

Claims 5, 10 and 11 are rejected as being based on an inadequate disclosure. Applicant has no support for "blending rocks and cement", for "contacting concrete", and for improving asphalt.

Claims 1 to 4, 8 and 9 are rejected as fully met by the Safford references.

Claims 5 to 7 are rejected as unpatentable over the Safford references in view of McLaughlin. Safford teaches exposing clay fillers (argillaceous rock consists of clay) to the vapors of organo-silicon halides to make them water-repellent. McLaughlin in column 13 teaches treating clay particles with silicone and incorporating them in cementitious material. No invention is seen in treating the clay with the Safford material and then incorporating it as aggregate in the McLaughlin process.

Claim 11 is rejected as unpatentable over the Safford references for the reason in the above paragraph in view of Sommer's method of making an asphalt emulsion.
Wagner is pertinent to explain the reaction of treating a silica containing material with a silicon halide gas.

No claim is allowed.

Examiner
C. Amending Patent

1. Letter to attorney

February 22, 1960

Dawson, Tilton, Fallon and Lungmus,
Attorneys at Law,
209 South La Salle Street,
Chicago 4, Illinois.

ATTENTION MR. FALLON.

Dear Mr. Fallon:

In your letter of December 10, 1959, to Mr. Quincy C. Ayres concerning the Hiltrop and Lemish Application Serial No. 828,682

you state that you believe that you can successfully argue formal matters—the form of claims, etc. That is very good and we shall leave that part of it entirely in your hands. Our comments will be limited, for the most part, to the pertinency of the references since, as you say, that is the more immediate problem.

Before going to the references, however, allow us to comment concerning the second paragraph, page 2, of the communication from the EXAMINER. We refer to the following paragraph.

Quote—

"Claims 5, 10 and 11 are rejected as being based on inadequate disclosure. Applicant has no support for 'blending rocks and cement,' for 'contacting concrete,' and for improving asphalt." End of quote.

We say:

Concerning claim 5; i.e., "blending rocks and cement".

Plates 9 and 10 below are offered as support for our claim that
Plate 9. Treated and untreated aggregate set in concrete.

Plate 10. Close-up of treated, left, and untreated, right, aggregate in concrete. Note visible reactions shells in untreated argillaceous aggregate.
contacting argillaceous rocks with a silicon halide gas and thereafter blending said rocks with cement, results in a more stabilized concrete.

The upper concrete bar in Plate 9 was prepared using various specimens of carbonate rock as aggregate. The lower bar was prepared from exactly similar rock specimens as is evidenced by similar specimen numbers. However, the rocks in the bottom bar were contacted with vapors of \((\text{CH}_3)_2\text{SiCl}_2\) and \(\text{CH}_3\text{SiCl}_3\) before being placed in the cement. Both bars were then placed in a warm water bath for 3 months. Bisque and Lemish (1958, 1959) have shown that such a period is long enough to bring about growth of "reaction shells". Furthermore, Bisque and Lemish (1961) have shown that the growth of such "reaction shells" leads to a decrease in the compressive strength of the concrete. The concrete bars of Plate 9 were prepared and pictures presented to show that untreated argillaceous aggregate grows "shells" and that silanated argillaceous aggregate does not. This fact is best demonstrated by the close-up view, Plate 10. A close-up view of rock specimen number 4 is presented. Treated rock on the left; untreated rock on the upper right. A reaction shell in the untreated argillaceous rock is evidenced by the presence of a dark rim in the rock on the upper right.

Concerning claim 10; i.e., "contacting concrete". Plate 8, of the original paper, which we mailed to you, is offered in support of our claim of a method of rendering hardened concrete
less susceptible to degradation. Plate 8 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 acid as contrasted to a non-treated specimen which readily effervesced and disintegrated.

In addition to the above support, the resistance to degradation by repeated freezing and thawing of treated and untreated concrete specimens are being compared. Preliminary investigations have shown that the treated specimens are more resistant. Quantitative data, collected under carefully controlled conditions are now being collected.

Concerning claim 11; i.e., "improving an asphalt-to-aggregate bond". Preliminary investigations have shown that treated aggregate is more readily wet by hot asphalt than is untreated aggregate. It is argued that such a result would be expected since the microsurface of the treated aggregate is essentially blanketed by an organic polymer. Experiments are being performed on carefully selected aggregate, under carefully controlled conditions, in order to collect quantitative data which will show the extent of improvement of bond brought about by contacting said aggregate with a silconhalide gas.

Now to turn to the remarks concerning the references:

1- Third paragraph, page 2, of the report from the
EXAMINER. "Claims 1 to 4, and 8 and 9 are rejected, etc., etc."

In the first place, Safford does not, in either patent, discuss carbonate rocks; nor does he discuss Portland cement or concrete made thereof.

Safford's patent number 2,510,661 teaches treating finely-divided inorganic materials in order to improve its water and humidity resistance, as well as improving the free-flowing property of said finely-divided material. Our claim is for treating, not finely-divided materials, but rather, the coarse aggregate (which may be as large as 1 inch in diameter) in order to prevent absorption of mobile silicon, by the rock, from the cement paste. Safford cites treating a particular clay mineral, (i.e., Catalpo clay) which is, indeed, finely-divided, and obtaining the results he desires. We teach treating carbonate aggregate, which might contain several different clay minerals in varying amounts as impurities, with vaporous organosilanes. We observe that, when such carbonate aggregate are treated as we suggest, they become water repellent throughout. This is because of the natural occurrence, throughout the rock, of minute, interconnected pore spaces. Further, we observe that, when such a carbonate rock is treated with vaporous silanes and then the carbonate leached away, the insoluble residue (impurity) in the rock has been linked together by a three dimensional polymer. Such a "linking together" is not observed by Safford in the case of pure clays and is, in fact, just the exact opposite effect which he claims and desires. It is only
in the case of carbonate rocks where such a "linking together" of the argillaceous material takes place. We hypothesize that the depositional environment, in which the carbonate rock accumulated at some distant time in the geologic past, was such as to allow very intimate mingling of the argillaceous particles. This very intimate and natural occurrence of the particles allows for three dimensional polymerization and subsequent linking together of said particles. Such linking together is evidenced by Plate 5 of our original paper and by the following data.

Table 6. Comparison of loss after freezing and thawing test

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Not treated</th>
<th>% Loss</th>
<th>Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glory 3</td>
<td>37</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Glory 6</td>
<td>36</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Glory 10</td>
<td>34</td>
<td>12</td>
<td></td>
</tr>
</tbody>
</table>

The data in Table 6 indicates the increased resistance to degradation by repeated freezing and thawing. The above specimens were each subjected to 16 cycles of freezing and thawing under standardized conditions. The degradation loss is several per cent less, in every case, when treated rock is compared with untreated rock.

Any argument put forward to show Safford's right to prior
claim by reason of patent number 2,563,555 is subject to exactly the same kind of rebuttal put forth above. For Safford, in that patent, once again, teaches the treating of finely-divided fillers (column 2, line 32) and subsequently placing such finely divided fillers (e.g., a clay mineral) into a heat convertible polymer.

Once again, we are teaching the treatment of a whole rock (not a specific mineral). Which rock has accumulated in such a manner and of such a composition as to provide the desired characteristics after having been treated by the vaporous silane. Once treated, the rock is incorporated into Portland cement or into asphalt to form a better concrete.

II- Fourth paragraph, page 2, - "Claims 5 to 7 are rejected as unpatentable over the Safford references in view of McLaughlin. Etc., etc."

We have already discussed our views of the Safford references.

Now concerning McLaughlin Column 13—Frankly we are unable to see the pertinency of this reference. McLaughlin shows a machine for subjecting clay to temperatures of several hundred degrees Fahrenheit. Once subjected to such a temperature, the clay is obviously not as it once was. It becomes an entirely new and different material. These "spherulized" particles (column 13) are then mixed with a commercial 50% silicone solution. This is entirely different from our approach. McLaughlin is using a solution of a SILICONE. We are using a vaporous
SILANE to treat a naturally occurring ROCK.

III- Fifth paragraph, page 2, - "Claim 11 is rejected, etc., etc."

Our rebuttal to Safford's prior claim has been stated above.

Now concerning Somner's method of making an asphalt emulsion. Somner teaches mixing a water soluble alkali-metal-silicate into an asphalt emulsion. That mixture is subsequently used for soil impermeabilization. Such a procedure has no connection with ours whatsoever. We treat the naturally occurring, rock aggregate with vaporous silanes. The treated aggregate is subsequently mixed with asphalt in a manner exactly similar to the old method employed in the art of preparing asphaltic concrete. The asphaltic concrete obtained, using our treated aggregate, is of superior quality.

IV- Second paragraph, page 3, - "Wagner is pertinent to explain the reaction of treating a silica containing material with a siliconhalide gas."

We say that Wagner's discussion is not pertinent to our patent. Wagner discusses a surface reaction between finely divided silica, having an extensive surface area, (column 1, line 19) and a chlorosilane. Chemically speaking, silica is SiO₂. Mineralogically it is not defined. Our patent involves the treatment of naturally occurring carbonate rock, which contains various quantities of various impurities.

Mr. Fallon, this ends our comments concerning the communi-
cation from the EXAMINER in charge of our application. We hope that you find the above comments useful when further arguing our right to patent.

We remain,

Very sincerely yours,

Carl L. Hiltrop
and
Dr. John Lemish
DEPARTMENT OF GEOLOGY
IOWA STATE UNIVERSITY
2. Letter from attorney

DAWSON, TILTON, FALLON & LUNGMUS
Attorneys at Law
209 South La Salle Street
Chicago 4, Illinois

March 9, 1960

Mr. Quincy C. Ayres,
Iowa State College Research Foundation,
108 Morrill Hall,
Ames, Iowa

Dear Quincy:

We enclose herewith copies of an amendment prepared in the Hiltrop and Lemish application, Serial No. 828,682, pertaining to Aggregate Treatment. The comments and suggestions of Mr. Hiltrop were very helpful, and you will see that they have been embodied in our remarks.

Very truly yours,

DAWSON, TILTON, FALLON & LUNGMUS
3. Amendments

IN THE UNITED STATES PATENT OFFICE

Application of:

CARL L. HILTROP

and

JOHN LEMISH

Serial No. 828,682

Filed July 22, 1959

AGGREGATE TREATMENT

Pat. Div. 56

Hon. Commissioner of Patents,
Washington 25, D.C.

Sir:

In response to Official action Paper No. 2, please enter
the following amendment:

In the specification:

Page 6, line 3, after "employed.», insert — As is apparent
from the foregoing, the treated rocks may be blended in conven­
tional fashion with cement to provide concrete and the treated
aggregate may also be advantageously used in other materials,
as in asphalt. --.

In the claims:

Claim 1, last line, after "gas», insert — to maintain the
acid-insoluble portion in a three dimensional configuration—.

Claim 5, last line, after "concrete", insert — whereby
the acid-insoluble moiety of the rock is maintained in a three
dimensional configuration --.

Claim 8, last line, after "halide", insert — to maintain
the acid-insoluble portion in a three dimensional configura­
tion —.
Claim 9, last line, after "gas", insert -- to maintain the acid-insoluble portion in a three dimensional configuration --.

Claim 10, line 1, after "concrete", insert -- containing a rock aggregate --; last line, after "gas", insert -- to maintain the acid-insoluble portion of the aggregate in a three dimensional configuration --.

Claim 11, last line, after "gas", insert -- to maintain the acid-insoluble portion of the aggregate in a three dimensional configuration --.

Reconsideration of this application is respectfully requested.

The foregoing amendment is directed to both the specification and claims. The amendment to the specification is believed to have overcome the objections set forth in the first full paragraph on page 2 of the above-identified Office action. The specification now calls for uniting cement with rocks to form concrete as well as blending asphalt in the rock aggregate, so that there is support for claims 5 and 11. The original claims, of course, form part of the specification, so that it is believed that the sentence introduced into the specification is proper. On page 6, the sentence beginning at line 8 deals specifically with the hardened concrete called for in claim 10.

The claims have been amended to better bring out the novelty of applicants' invention and now define the character of the rocks in so far as the acid-insoluble moiety is concerned. This portion of the rock is specified to be maintained at its
original three dimensional configuration, and applicants teach this in the last full paragraph on page 5 of their specification. Relative to the completeness of the claims, it is respectfully submitted that so long as the claims teach one skilled in the art, there is an adequate disclosure. This is what the claims do here. Relative to indefiniteness, it is established that the later practitioner may be required to perform some routine experimentation to achieve optimum results. That the claims, therefore, need not be "cook-book" style directions.

The prior art teachings having to do with clays are believed inadequate to teach one skilled in the art how to improve rock aggregate employed in concrete. In concrete, the impurities in the rock aggregate tend to collapse (i.e., lose their three dimensional configuration), and thus weaken the concrete. Through the inventive procedure, this is avoided. There is no teaching of this nature in either of the Safford patents, Safford being concerned with treating powders or finely-divided products so as to maintain them free-flowing, and does not deal with carbonate rocks, Portland cement or concrete in either patent. In fact, it is believed that the teaching of Safford would lead one skilled in the art away from applicants' invention, Safford not desiring the "linking together" of particles to get a three dimensional configuration.

To this, McLaughlin brings nothing of relevance, since McLaughlin is not concerned with a concrete aggregate in the
portion of his teaching having to do with treating materials with a silicone. Starting at column 13, McLaughlin, in dealing with concrete and cement, merely uses his fused product, not one that has not been treated with a silicone-containing gas. At the very best, McLaughlin's teaching would tend to obscure the issue, and it is only after applicants' teaching has been consulted that there can be any relationship established between McLaughlin and Safford.

Sommer teaches mixing a water-soluble alkali-metal-silicate into an asphalt emulsion for soil impermeabilization. This is a far cry from applicants' procedure and again, its only relevancy, if any, appears after one is versed with applicants' teaching. Wagner also leads away from applicants' teaching because of his concern with finely-divided silica.

In view of the foregoing, reconsideration and favorable action on the amended application are respectfully solicited.

Very respectfully,

DAWSON, TILTON, FALLON & LUNGMUS
By Jerry Fallon

Chicago 4, Illinois
March __, 1960