

Reactivity of Treated and Untreated Marble in Carbon Dioxide Atmospheres

K. L. GAURI, PREEYAPORN TANJARUPHAN,
MADIRAJU APPA RAO, AND THORNTON LIPSCOMB

University of Louisville, Louisville, Kentucky 40208

ABSTRACT

Marble specimens were impregnated with certain epoxies and fluorocarbon-acrylic copolymers. The treated and untreated specimens were exposed to, while immersed in deionized water, 0.983, 6.2, 8.28, and 11.02 percent $p\text{CO}_2$ at 20 C in a dynamic system. The concentration of leached Ca^{2+} in the water was determined by EDTA titrations and atomic absorption. The values obtained by those methods were nearly identical. The rate of reaction was based on the increment in Ca^{2+} concentration as a function of time. The equilibrium constant K , calculated from the experimental data, had a value of 1.49×10^{-6} , and compared well with the value of 1.58×10^{-6} given by Garrels and McKenzie (1971). Specimens treated with fluorocarbon-acrylic compounds revealed only one-half reactivity relative to untreated specimens in the initial phases of reaction. Certain epoxies provided protection, other epoxies actually enhanced the rate of reaction. It is proposed that pertinent data generated in the course of this study be used as a basis for quantitative performance criteria for stone and concrete preservative treatments.

INTRODUCTION

Carbon dioxide is a prominent agent of stone decay. When dissolved in water, carbon dioxide (CO_2) generates hydrogen (H^+) ions that are responsible for dissociation of calcareous and silicate minerals, essential ingredients of most building stones.

The equilibrium concentration of CO_2 in water is a function of temperature and its partial pressure in the atmosphere. The past 100 years have witnessed an increment of 13 percent in the CO_2 budget of the atmosphere due to an increase in the combustion of fossil fuels (Bolin and Erickson 1959). That situation has necessitated development of preservative materials and methods for building stones. But, while such materials and methods have multiplied, the development of criteria for their performance has lagged behind seriously. One of the purposes of this paper is to present means to preservation technologists for a rapid laboratory evaluation of proposed preservative treatment against CO_2 attack. Another purpose of this paper is to show that careful laboratory testing of preservative materials is necessary to determine whether a given material will provide

protection since it is likely that certain so-called preservatives may enhance the reactivity.

In our continuing studies since 1970 on deterioration and preservation of stone, we have reported earlier on sulfur dioxide-calcite reactivity (Gauri et al. 1973, Gauri and Sarma 1973), on the usefulness of certain industrial resins as stone preservatives (Gauri 1974b, Gauri et al. 1973, 1974), on a technique for in-depth impregnation (Gauri 1970, U. S. Patent 1974), and on comparative physical properties of certain treated and untreated calcareous stones (Gauri 1974a, Gauri et al. 1974). This supplements our earlier studies, and has yielded data for determining the equilibrium constant of CO_2 - CaCO_3 reactions. Inferences have been drawn from this study to show that the initial reaction rate rather than the equilibrium concentration is useful in predicting the CO_2 - CaCO_3 reactivity in the ambient.

ACKNOWLEDGMENTS

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the use of their Atomic Absorption Spectrometers.

MATERIALS

The test samples were rectangular blocks, $4.5 \times 3.2 \times 0.5$ cm, cut from Alabama white and Vermont green marbles. Those marble species were selected because of their higher reactivity with chemically active gases. The final grinding finish on the blocks was obtained with 400-grit silicon carbide powder. The specimens were cleaned ultrasonically; the control was cleaned before exposure to concentrated atmosphere, and other specimens were cleaned before treatment.

TREATMENT

The experimental specimens were treated with epoxies such as aliphatic diepoxides and bisphenol-A diglycidal ether. Fluorocarbons and acrylics also were used for treatment. Treatment varied from surface coatings to in-depth impregnations. While the surface coatings were made by short-term immersion or brushing of polymers, the in-depth impregnations were obtained by sequential immersion of specimens in polymer-solvent mixtures of increasing polymer concentration (Gauri 1970, U. S. Patent 1974). Specifically, the treatments for each kind of marble were:

Specimen A.—Treatment with bisphenol-A epoxy resin: immersion in acetone, 10 min, followed by immersion in 50 percent and 80 percent epoxy solution in acetone, 20 min each.

Specimen B.—Treatment with bisphenol-A epoxy resin: immersion in acetone, 10 min, followed by immersion in 50 percent epoxy solution in acetone, 30 min.

Specimen C.—Treatment with bisphenol-A epoxy resin followed by coating with a fluorocarbon: immersion in acetone, 10 min, followed by immersion in 50 percent epoxy; surface cleaned with acetone; after epoxy polymerization surface coated with 15 percent fluorocarbon in methyl ethyl ketone (MEK).

Specimen D.—Treatment with aliphatic

diepoxide: immersion in 50 percent epoxy in acetone, 30 min.

Specimen E.—Control.

Specimen F.—Treatment with aliphatic diepoxide: immersion in absolute epoxy, 20 min.

Specimen G.—Treatment with fluorocarbon-acrylic copolymer: immersion in 2.5 percent resin in 1:1 MEK-cellusolve acetate, 10 min, followed by immersion in 15 percent resin, 10 min.

The bisphenol-A epoxy and the aliphatic diepoxide were obtained from Celanese Speciality Coatings, P.O. Box 857, Louisville, Ky. 40201; the fluorocarbon and the acrylic were obtained from E. I. Dupont de Nemours & Company, Inc., Wilmington, Del. 19898.

EXPERIMENTAL SETUP

All specimens, both treated and untreated, were completely immersed in deionized water for a minimum of 24 hours to insure that they did not absorb water when exposed to CO_2 atmosphere in an immersed state. The experimental work was conducted in 2 phases: (1) the Vermont green marble was immersed in 20 ml of water in a 50-ml beaker such that about half of the specimen was immersed while the other half was above water, and (2) the sample of Alabama white marble was completely immersed in 45 ml of water. Then specimens were placed in the reaction chamber (Fig. 1). After a known period of time, as given in respective figures, the beakers were removed and analyzed for Ca^{2+} ion by titrating a known volume of sample with standard EDTA solution using Eriochrome Black T as an indicator. The total Ca^{2+} ion concentration in the case of the half-submerged specimen for a given period of time is lower than that of a fully immersed specimen. The results, however, are comparable within each phase of the work. Magnesium chloride solution was added before the titration for a better resolution of the endpoint. The volume of EDTA required to neutralize the Mg^{2+} ions was subtracted from

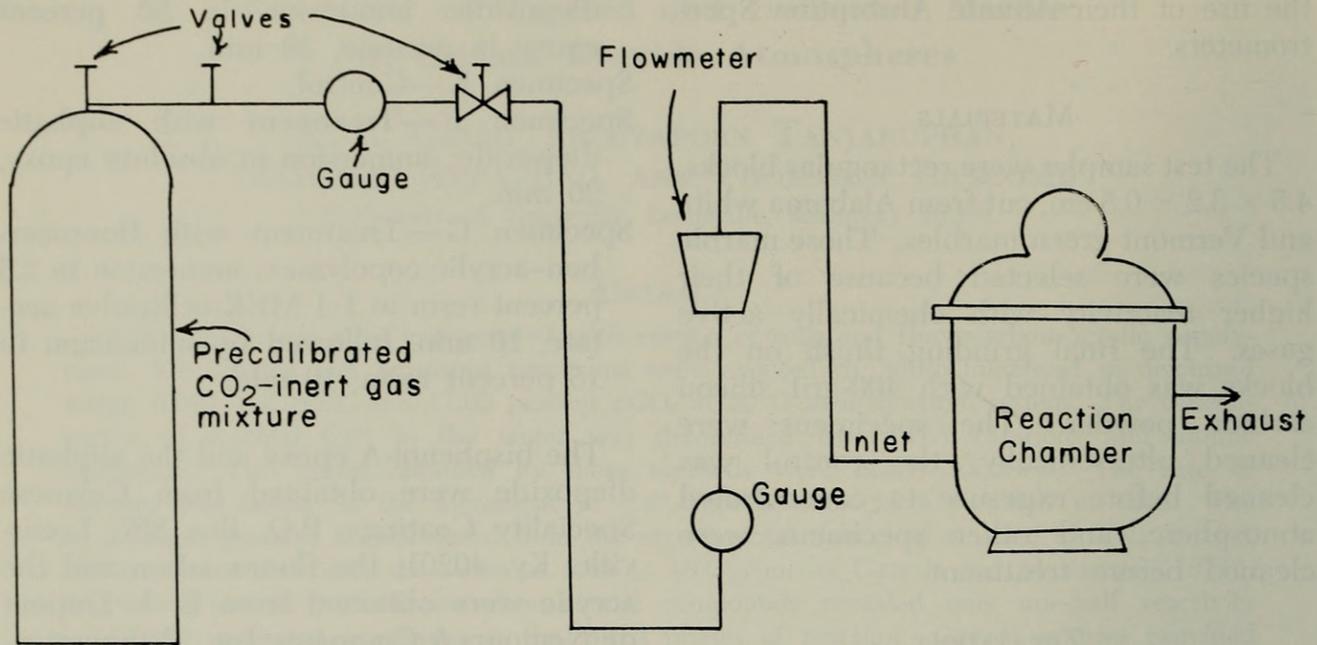


FIG. 1. Schematic detail of dynamic reaction chamber.

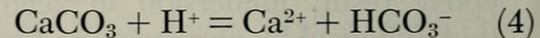
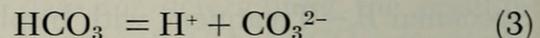
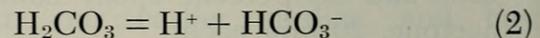
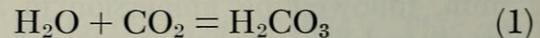
the total titer value. The Ca^{2+} ion concentration also was determined by atomic absorption for some runs, and the results obtained by both methods agreed to within 5 percent. The temperature throughout the reaction was maintained at 20 C. The experiment was repeated for various time periods and the concentration of Ca^{2+} ions was plotted as a function of time (Figs. 2-6). The concentration of CO_2 in the cylinder was determined by absorbing CO_2 in ascarite (Hamilton and Simpson 1952: 351). The cylinders with known CO_2 concentration in air or nitrogen were provided by Air Products and Chemicals Inc., 733 West Broad Street, Emmaus, Pa. 18049, who determined the CO_2 concentration by gas chromatography. The CO_2 concentration was checked both at the entrance of the gas in the reaction chamber as well as at the exit by the standard method of reacting the gas with ascarite. A fairly small concentrational difference between the gas at the entrance and the exit was maintained by exposing only a small number of specimens in the reaction chamber.

REACTION KINETICS

Extensive studies have been conducted on the calcium carbonate-carbon dioxide-

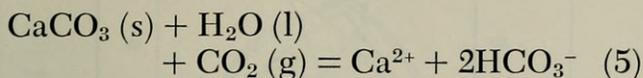
water reactions. The study by Miller (1952), though conducted for the geological implications of this reaction, is outstanding for several reasons; it includes a comprehensive literature survey on the subject, and it contains experimental work on 3 different sources of CaCO_3 with distilled water, NaCl solution, and sea water used as solvent. It also contains data on CaCO_3 solubility as a function of temperature and CO_2 pressure.

Some of the reactions taking place in the $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system could be written as:



Hougen et al. (1959:1062-1069) considered several other possible reactions and plotted the concentration of Ca^{2+} , HCO_3^- , CO_3^{2-} , H^+ , OH^- , and $\text{H}_2\text{CO}_3(\text{aq})$ as a function of the partial pressure of CO_2 . They concluded that at CO_2 pressures above 10^{-4} atmospheres the concentrations of (OH^-), (CO_3^{2-}), and (H^+) were negligible in comparison to the Ca^{2+} , HCO_3^- , and H_2CO_3 . In that range, they proposed that

the reaction takes place according to the stoichiometric equation:



This equation could also be obtained by combining Equations 1, 2, and 4. Equation 3 was neglected since there was no detectable trace of CO_3^{2-} as ascertained by titrating with HCl using the double indicator method.

The equilibrium constant for Equation 5 may be written as:

$$K = \frac{(a\text{Ca}^{2+})(a\text{HCO}_3^-)^2}{(a\text{CO}_2 (g))} \quad (6)$$

Since this deals with very dilute solutions, the activities can be replaced by the respective concentrations. Also by replacing $a\text{CO}_2$ by the partial pressure of CO_2 the equation can be written:

$$K = \frac{(\text{Ca}^{2+})(\text{HCO}_3^-)^2}{p\text{CO}_2} \quad (7)$$

From the stoichiometry of the equation we have $2(\text{Ca}^{2+}) = (\text{HCO}_3^-)$. Hence, Equation 7 becomes:

$$K = \frac{4(\text{Ca}^{2+})^3}{p\text{CO}_2} \quad (8)$$

As shown in Fig. 2, the Ca^{2+} concentration increased with time, asymptotically reaching the equilibrium value. That equilibrium value of Ca^{2+} was substituted in Equation 8 and the value of K was calculated for each CO_2 pressure (Table 1). The average value of equilibrium constant, K , is 1.49×10^{-6} . Garrels and McKenzie (1971) reported a value of 1.58×10^{-6} for reaction at room temperature. Hougen

TABLE 1.—REACTIVITY OF CALCITE IN CO_2 ATMOSPHERES OF VARIABLE CONCENTRATIONS

$p\text{CO}_2$	Ca^{2+} $\mu\text{g}/\text{ml}$ at equilibrium	$K = \frac{4(\text{Ca}^{2+})^3}{p\text{CO}_2}$
9.83×10^{-3}	62.8	1.57×10^{-6}
6.20×10^{-2}	113	1.45×10^{-6}
8.28×10^{-2}	121	1.34×10^{-6}
11.0×10^{-2}	141	1.59×10^{-6}

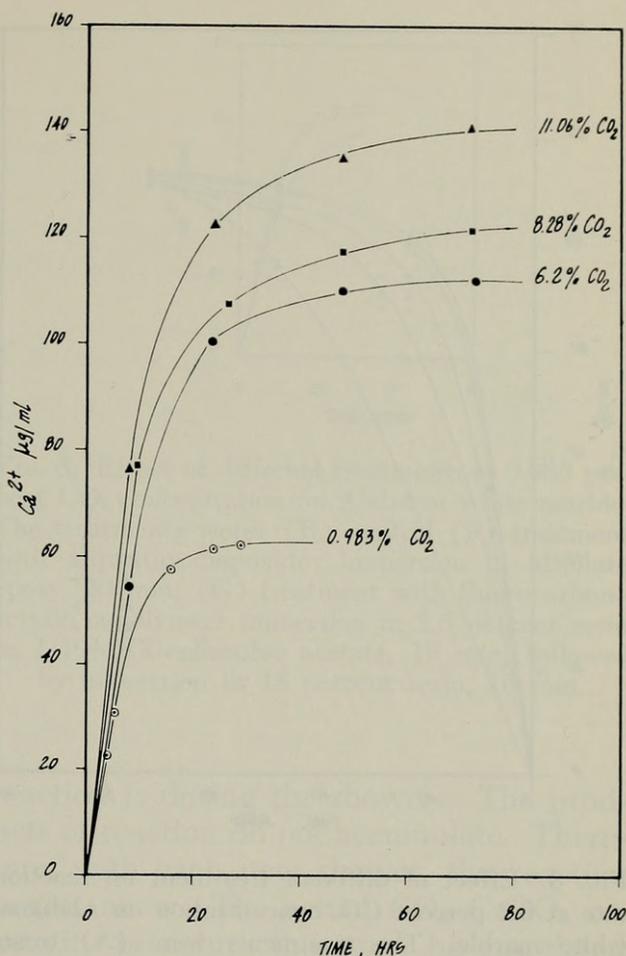
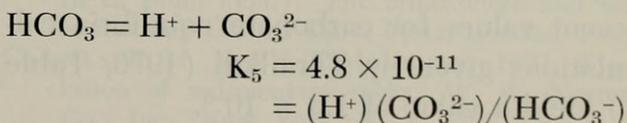
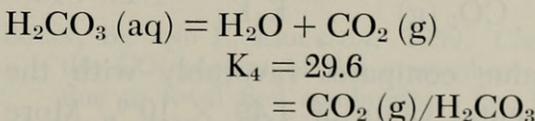
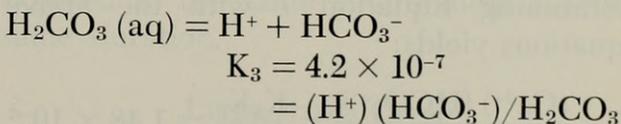
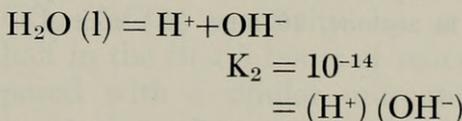
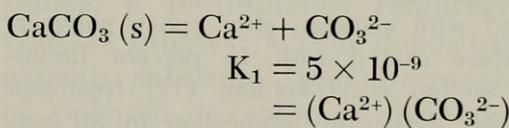


FIG. 2. Reaction rate for untreated Vermont green marble specimens at different CO_2 partial pressures.

et al. (1959) obtained a value of 0.6×10^{-6} from thermodynamic calculations. They selected the following reactions:



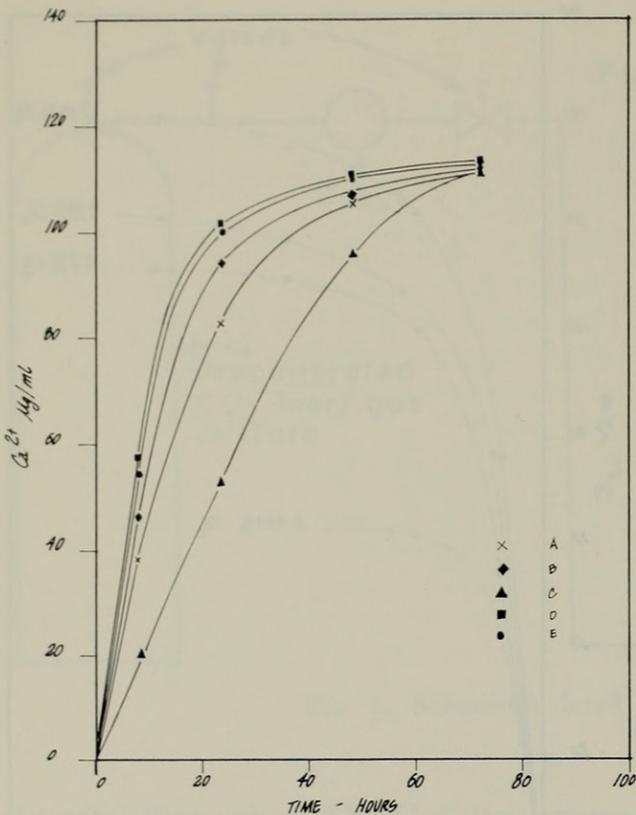


FIG. 3. Effect of different treatment on reaction rate at 6.2 percent CO_2 concentration on Alabama white marble. The treatments were (A) treatment with bisphenol-A epoxy resin: immersion in acetone, 10 min followed by immersion in 50 percent and 80 percent epoxy solution in acetone, 20 min each; (B) treatment with bisphenol-A epoxy resin: immersion in acetone, 10 min, followed by immersion in 50 percent epoxy solution in acetone, 30 min; (C) treatment with bisphenol-A epoxy resin followed by coating with a fluorocarbon: immersion in acetone, 10 min, followed by immersion in 50 percent epoxy; surface cleaned with acetone; after epoxy polymerization surface coated with 15 percent fluorocarbon in methyl ethyl ketone; (D) treatment with aliphatic diepoxide: immersion in 50 percent epoxy in acetone, 30 min; (E) control.

Combining Equation 7 with the above equations yields:

$$K = \frac{(\text{Ca}^{2+})(\text{HCO}_3^-)^2}{\text{CO}_2(\text{g})} = \frac{K_1 K_3}{K_4 K_5} = 1.48 \times 10^{-6}$$

This value compares favorably with the experimental value of 1.49×10^{-6} . More recent values for carbonate equilibria calculations given by Thrailkill (1976, Table 1) yield a value of 1.6×10^{-6} .

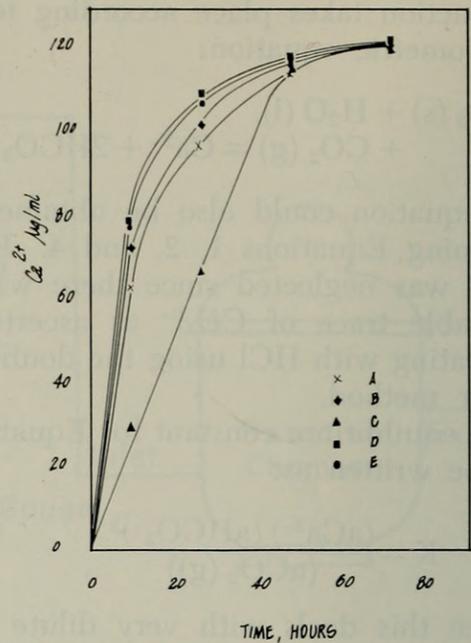


FIG. 4. Effect of different treatments at 8.28 percent CO_2 concentration on Alabama white marble. The treatments were the same as in Fig. 3.

RESULTS AND DISCUSSION

This study has produced the following significant results:

1. Treatment with certain polymers, e.g., bisphenol A type epoxies, acrylics, and fluorocarbons provided protection to the marble blocks, but the treatment with aliphatic diepoxide increased CO_2 - CaCO_3 reactivity in the earlier runs of reactions.

The increased CO_2 - CaCO_3 reactivity for specimens treated with aliphatic diepoxide is parallel to results previously reported for SO_2 - CaCO_3 reactivity (Gauri and Sarma 1973). The increased reactivity may be due to absorption of CO_2 by the polymer film, as in the case of SO_2 , or due to the polymer film acting as a semipermeable film to CO_2 permeation. We have determined experimentally that the aliphatic diepoxide film does not absorb CO_2 . The other likely explanation then is that CO_2 permeates selectively through the polymer film and thus builds a larger concentration at the calcite-polymer interface. The CO_2 concentration outside the film remains constant. This phenomenon, i.e., the concentration of CO_2 at polymer- CaCO_3 interface, must have been of a shorter

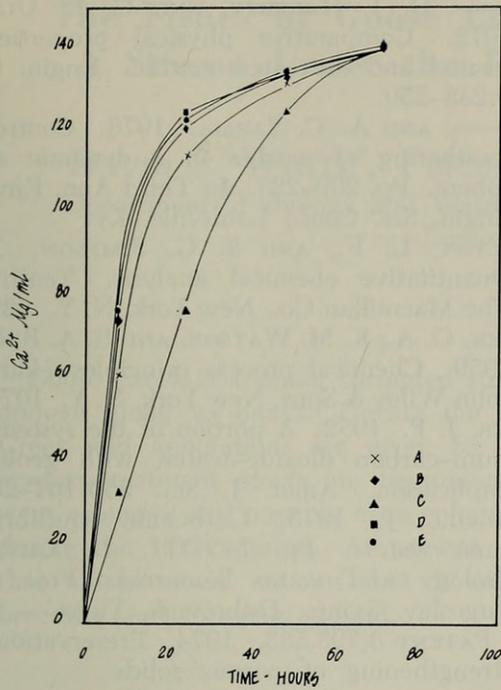


FIG. 5. Effect of different treatments at 11.06 percent CO_2 concentration on Alabama white marble. The treatments were the same as in Fig. 3.

duration because the reaction equilibrium of treated and untreated marble occurred at the same level of Ca^{2+} concentration. The reduced initial CO_2 - CaCO_3 reactivity of other treated specimens probably is due to the reduced rate of water absorption as given in the following section.

2. Marble specimens treated with the same polymer but with in-depth impregnation initially showed lesser reaction than those with shallow impregnation or those with no treatment at all. The phenomenon seems directly related to the rate of water movement into the specimen. The impregnation, by partially causing closure of certain pores and partially by being of water repellent materials, reduces the capillary movement of water into the stone. Yet in the long run, so much calcite is available that the reaction finally reaches equilibrium.

By corollary of the above, considerable protection can be provided to the stone by drastic reduction in the rate of flow of water. In nature, other than upward migration of ground water, the water of consequence for CO_2 - CaCO_3 reactivity is rainwater. The approximate duration of the

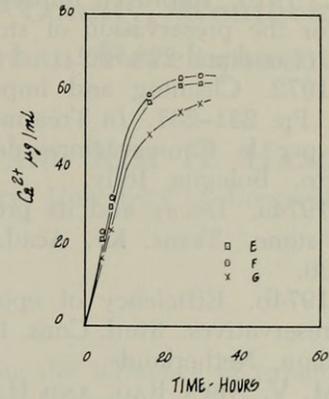


FIG. 6. Effect of different treatments at 0.983 percent CO_2 concentration on Alabama white marble. The treatments were: (E) control (F) treatment with aliphatic diepoxide: immersion in absolute epoxy, 20 min; (G) treatment with fluorocarbon-acrylic copolymer: immersion in 2.5 percent resin in 1:1 MEK-cellusolve acetate, 10 min, followed by immersion in 15 percent resin, 10 min.

reaction is during the showers. The products of reaction do not accumulate. Therefore, with each new shower, the reaction begins anew. The actual CO_2 - CaCO_3 reactivity in nature thus may be correlated with the initial reaction rate. The treatments, especially in-depth impregnation, therefore are very useful in retarding CO_2 - CaCO_3 reactivity.

3. The comparisons of reaction rates in the initial phases of reaction may form the basis for performance criteria of treatments for calcareous stone and concrete. For instance, a performance requirement may read as follows: a film deposited on calcareous substrate from 10 percent solids of polymer in solution shall reduce the CO_2 - CaCO_3 reactivity by at least one-half in the first 5 hours of reaction as compared with a similar untreated specimen exposed in the same environment for the same duration.

LITERATURE CITED

- BOLIN, B., AND E. ERICKSON. 1959. Changes in the CO_2 content of the atmosphere and sea due to fossil fuel combustion. Pp. 130-142. In B. Bolin (Ed.). The atmosphere and sea in motion. Oxford Univ. Press, London, Eng.
- GARRELS, R. M., AND F. T. MCKENZIE. 1971. Evolution of sedimentary rocks. W. W. Norton Co., Inc. New York, N. Y. 397 pp.

- GAURI, K. L. 1970. Improved impregnation technique for the preservation of stone statuary. *Nature* (London) 228:882.
- . 1972. Cleaning and impregnation of marble. Pp. 231-237. *In* Treatment of stone, Centro per la Conservazione delle Sculture All'aperto. Bologna, Italy.
- . 1974a. Decay and its preservation in natural stone. *Trans. Ky. Acad. Sci.* 35(1-2):29-36.
- . 1974b. Efficiency of epoxy resins as stone preservatives. *Stud. Cons.* 197:100-101. Amsterdam, Netherlands.
- , M. V. APPA RAO, AND H. J. GADIJAR. 1974. Certain epoxies, silicones, and vinyls as stone preservatives. P. 750. *In* Symposium on preservation of stone. *Geol. Soc. Amer.* 1974 Ann. Meet. (abs.).
- , G. C. DODERER, N. T. LIPSCOMB, AND A. C. SARMA. Reactivity of treated and untreated marble specimens in an SO₂ atmosphere. *Stud. Cons.* 18:25-35. Amsterdam, Netherlands.
- , D. J. HAGERTY, AND C. R. ULRICH. 1972. Comparative physical properties of treated and untreated marble. *Engin. Geol.* 6:235-250.
- , AND A. C. SARMA. 1973. Controlling weathering of marble in a dynamic atmosphere. Pp. 209-223. *In* Third Ann. Environ. Engin. Sci. Conf., Louisville, Ky.
- HAMILTON, L. F., AND S. G. SIMPSON. 1952. Quantitative chemical analysis. Tenth Ed. The Macmillan Co., New York, N. Y. 529 pp.
- HOUGEN, O. A., K. M. WATSON, AND R. A. RAGATZ. 1959. Chemical process principles (Part 2). John Wiley & Sons, New York, N. Y. 1072 pp.
- MILLER, J. P. 1952. A portion of the system calcium-carbon dioxide-water, with geological implication. *Amer. J. Sci.* 250:161-203.
- THRAILKILL, J. 1975. Carbonate equilibria in karst waters. Pp. 745-771. *In* Karst hydrology and water resources. Proc. US-Yugoslav. Symp., Dubrovnik, Yugo.
- U. S. PATENT 3,795,533. 1974. Preservation and strengthening of porous solids.



Gauri, K. Lal, Tanjaruphan, Preeyaporn, and Rao, Madiraju Appa. 1977.
"Reactivity of treated and untreated marble in carbon dioxide atmospheres."
Transactions of the Kentucky Academy of Science 38(1-2), 38-44.

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