

USE OF COUPLED PASSIVANTS AND CONSOLIDANTS
ON CALCITE MINERAL SURFACES

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ABSTRACT

Deterioration of monuments, buildings, and works of art constructed of carbonate-based stone potentially can be arrested by applying a combination of chemical passivants and consolidants that prevent hydrolytic attack and mechanical weakening. We used molecular modeling and laboratory synthesis to develop an improved passivating agent for the calcite mineral surface based on binding strength and molecular packing density. The effectiveness of the passivating agent with and without a linked outer layer of consolidant against chemical weathering was determined through leaching tests conducted with a pH-stat apparatus at pH 5 and 25°C. For the range of molecules considered, modeling results indicate that the strongest-binding passivant is the trimethoxy dianionic form of silylalkylaminocarboxylate (SAAC). The same form of silylalkylphosphonate (SAP) is the second strongest binder and the trisilanol neutral form of aminoethylaminopropylsilane (AEAPS) is ranked third. Short-term leaching tests on calcite powders coated with the trisilanol derivative of SAAC, the triethoxy neutral form of SAP, and the trimethoxy neutral form of AEAPS show that the passivant alone does not significantly slow the dissolution rate. However, all passivants when linked to the sol consolidant result in decreased rates. Combined AEAPS plus consolidant results in a coating that performs better than the commercial product Conservare® OH and at least as well as Conservare® H. The modeling results indicate that there may be a threshold binding energy for the passivant above which the dissolution rate of calcite is actually enhanced. More strongly-binding passivants may aid in the dissolution mechanism or dissociate in aqueous solution exposing the calcite surface to water.

INTRODUCTION

Suitable protective coatings for monuments, sculptures, and buildings constructed of carbonate stone require improved adhesion between the carbonate substrate and alkoxy silane consolidants [1]. Here, we report on the efficacy of such adhesive agents designed through a combined approach of modeling their adhesive and passivating properties using computations at the molecular scale and testing those properties during simulated leaching tests in the laboratory.

Three candidate passivant molecules were selected based on their potential bonding configurations with surfaces of calcite (CaCO_3): (1) silylaminocarboxylates (SAAC) with three carboxylate ligands, (2) silylphosphonates (SAP) with two strong P-O bonds, and (3) aminoethylaminopropylsilanes (AEAPS) with two nitrogen-based ligands. All three classes have a silanol tail that can combine with an alkoxy silane consolidant which can provide mechanical and UV stability (Figure 1). Passivants were applied to calcite powders in single or multiple coatings with and without a coating of an alkoxy silane consolidant in order to test their potential for retarding dissolution under simple simulated weathering conditions. Our goals were (1) to test the

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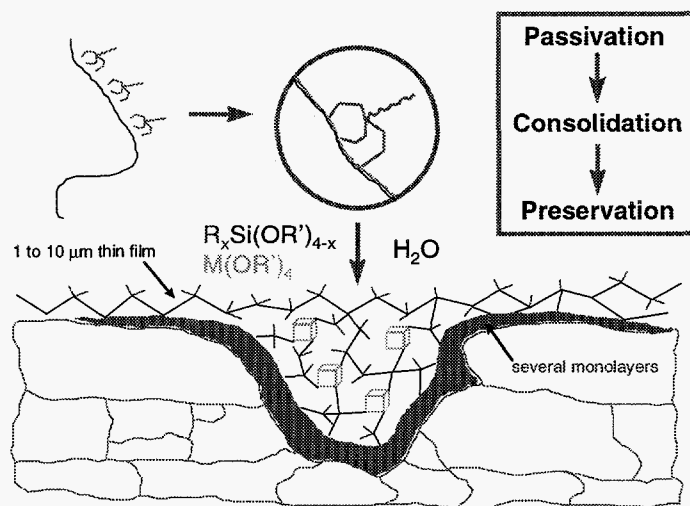


Figure 1. Schematic diagram of a crevice in a limestone sculpture, coated with the passivant (shaded layer) plus alkoxy silane consolidant (1 to 10 μm outer thin film). The sketch in the upper left shows a tridentate passivant (e.g., SAAC) attached to the surface of the sculpted "nose." Si and Zr oxides (e.g., $\text{M}(\text{OR}')_4$) can be added to the alkoxy silane layer to increase mechanical strength and limit shrinkage.

usefulness of molecular modeling for predicting effective passivants against their actual performance in aqueous environments at 25°C, and (2) to demonstrate that a combined passivant/consolidant material is capable of protecting carbonate-based rocks from weathering.

METHODS

Computational Models

Molecular modeling was used to evaluate the suitability of candidate passivants and several derivative structures for binding to calcite mineral surfaces. The total energy of the chemical system was monitored as a function of the atomic positions based on the energy contributions of bond stretching, bending, and torsion of the passivant molecule and the nonbonded interactions (Coulombic, short-range repulsive, and van der Waals). Energy-minimized configurations were first obtained for the isolated passivant molecule (Figure 2), and then allowed to re-equilibrate under the influence of a calcite surface. The common (104) and (100) cleavage surfaces of calcite were created as periodic 29 Å x 29 Å lattices with a surface spacing of 25 Å. All atoms were constrained to their observed structural positions with the calcium ion maintained at its full ionic charge (+2) and the carbonate charge (-2) partitioned among carbon (0.919) and oxygen (-0.973). Since the passivant solutions are typically applied to the stone at fairly high pH's, the exposed calcite surface is expected to be dominated by Ca^{2+} and CO_3^{2-} [2].

The computer simulations suggest that SAAC has the strongest binding to the calcite (104) surface (Figure 3); SAP is slightly less-strongly bound compared to SAAC. The calculated binding energy of a TEOS (tetraethoxysilane) monomer is considerable lower than SAAC and SAP, but has a slightly larger value than that observed for AEAPS. Typically, the binding energy of the dianion is greater than the monoanion, which in turn is greater than the neutral passivant. Relative to the alkylsilane group of the passivant, the molecular models indicate that, generally, the binding energy decreases from the trimethoxy derivative, to triethoxy, and to trihydroxy. Similar trends in relative binding energy of the passivants were observed for the calcite (100) and (104) surfaces; however, the binding energies are somewhat smaller for (100).

Energy-Optimized Structures

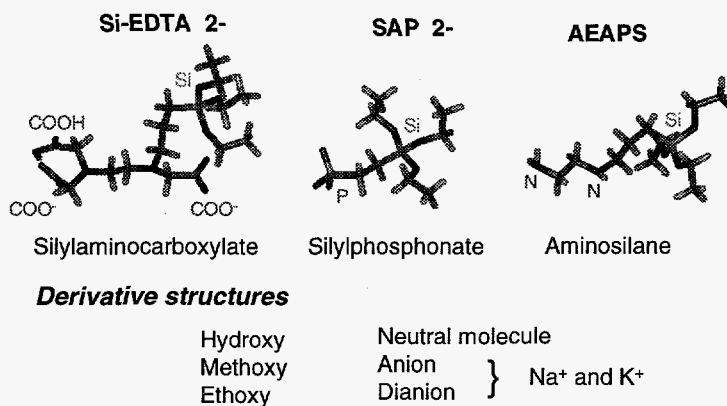


Figure 2. The three candidate passivant classes and a listing of their derivatives with respect to the silane tail (left) and form of the passivant molecule that reacts with the surface (right).

Monte Carlo simulations of the sequential packing of individual passivant molecules onto the calcite (104) surface help to evaluate the expected surface coverage of the molecules. The simulations rely on a random sampling of a 29 Å x 29 Å x 25 Å volume such that a packing configuration is not accepted unless the energy falls below a critical value. Ten separate packing simulations using four passivant molecules each were performed, followed by energy minimization of the molecules. The final lowest energy configurations show surface coverage of passivants ranging from 175 to 210 Å² per molecule (all triethoxy derivatives). SAP provides the greatest coverage per molecule, followed by SAAC, then AEAPS. These packing results provide a quantitative basis for the preparation of solution concentrations and optimum number of coatings to ensure a complete coating of passivant on the stone surface.

Experiments

Candidate passivant solutions were prepared by dilution in methanol. Calcite powder (Aldrich, low alkali CaCO₃) was pretreated to remove fines by adding an excess volume of

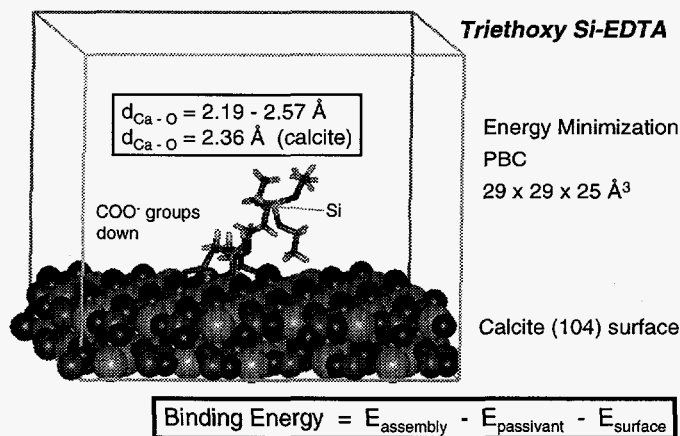


Figure 3. Molecular model showing binding configuration of triethoxy-Si-EDTA (SAAC) molecule to common cleavage surface of calcite (CaCO₃).

methanol, ultrasonicing 5 min, decanting the methanol, and air drying at 50°C. Ten grams of CaCO₃ was added to 40 ml of passivant solution while stirring. The solution was ultrasonically treated for 2 min to promote complete wetting of the powder and minimize agglomeration. The passivant/powder solution was stirred at room temperature for at least 30 min. and vacuum filtered through a 1 micron teflon filter. The filter cake was gently broken up and allowed to dry at 50°C. For multiple coatings, the dried powder was resuspended in the passivant solution and the process repeated. Following several coatings at high passivant concentrations (*i.e.*, 25 wt%), filtration through a 10 micron filter was necessary.

A sol-gel derived consolidant was chosen from a family of silica sols prepared using a one- or two-step acid catalysis procedure [3]. These sols are formulated to promote maximum condensation and have been developed for gas separation applications because of their tailored microporosity. The chosen consolidating coating is a nominal 50 wt% silica solution which was partially hydrolyzed under acidic conditions to initiate polymerization.

After separating the passivated powder from the passivant solution, the damp powder was resuspended in consolidant solution to encourage polymerization between the reactive termini of the passivating molecule and the alkoxy silane consolidants. The suspension was treated ultrasonically for 2 min and stirred for 30-60 min at room temperature. Following filtration through a 1 µm teflon filter, the powder was dried under ambient conditions to encourage further reaction with atmospheric moisture.

Coated and uncoated calcite powders were dissolved under controlled conditions in pH-stat experiments [4] at 25°C (Figure 4). The aqueous solution was bubbled constantly with 20% CO₂ in N₂ to facilitate pH control at pH = 5, representing a mildly acidic rain. After adding 0.25 g of calcite (0.358 m²/g) to the pre-equilibrated stirred solution, the pH was adjusted to 5 by the dissolution process and by base (0.1 N NaOH) addition. Then the pH was maintained to within ± 0.01 pH units by constant addition of 0.1 N HCl at a rate proportional to the rate of calcite dissolution. Total elapsed time of an experiment was at least 30 minutes.

RESULTS AND DISCUSSION

Dissolution rates from 24 experiments with three candidate passivants are given in Table 1 and Figure 5. A number of observations can be made. First, the order of effectiveness is reversed from that predicted using the relative binding energies determined by molecular modeling.

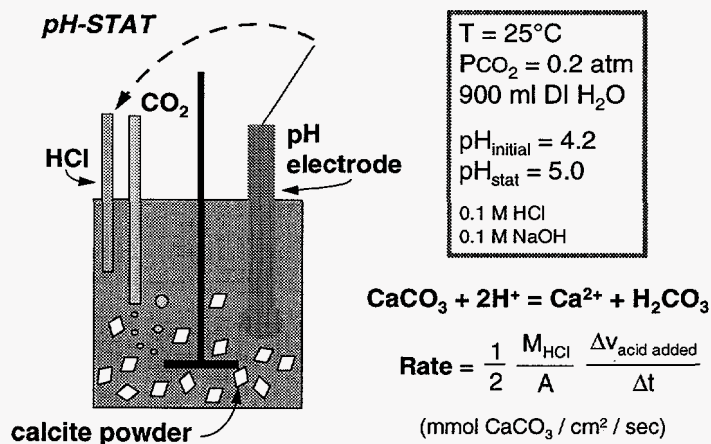


Figure 4. Schematic diagram of pH-stat apparatus and calculation of dissolution rate.

Second, neither single nor multiple coatings of the passivants alone significantly reduce the rate of calcite dissolution. Third, all passivants when linked to a single coating of the sol consolidant result in slower dissolution rates. The most significant decrease occurs with the AEAPS passivant. Fourth, the effectiveness of the passivant in binding to the consolidant is higher when the passivant is applied from a higher concentration solution. Fifth, the AEAPS passivant plus consolidant (50% TEOS) combination is more effective than the commercial product Conservare® OH (~ 75% TEOS from Wacker Chemie), and at least as, if not slightly more, effective than Conservare® H which includes a hydrophobic agent. Neither commercial product is recommended for treatment of carbonate stone. In comparing these results, we note that we devised a coating procedure for powders, and therefore, could not follow exactly the recommended procedures for application of Conservare® OH and H onto carbonate stone. However, our procedures were used consistently for all materials. Sixth, multiple coatings of consolidant, as exemplified by the Conservare® H-coated samples, appear to reduce the effectiveness against dissolution.

The trend in dissolution rates contradicts the trend of the model predictions for passivant binding strength. This suggests a threshold binding energy above which the passivant enhances the dissolution rate. Interestingly, the calculated binding energy for TEOS, the primary component of our sol-gel and both commercial consolidants, lies between that of SAP and AEAPS. Similarly, the measured dissolution rate for calcite powder coated with Conservare® OH also lies between the rates for powders coated with SAP + consolidant and AEAPS + consolidant. The consolidant appears to play a role in inhibiting dissolution because all of the combination coatings acted to reduce dissolution rate. Although the binding energy of AEAPS is less than those of SAAC and SAP, AEAPS binds strongly enough to yield a new material that reduces the dissolution rate significantly. AEAPS is also commercially-available and relatively inexpensive.

CONCLUSIONS

Molecular models combined with dissolution experiments constitute a rational approach for designing new materials for protection of carbonate-based structures and sculptures. Calculations

Table I. pH-stat experiments. Rates are in units of mmol/cm²/sec and have uncertainties of 20%.

Experiment #	Passivant	# of Coats	Consolidant	# of Coats	Log Dissolution Rate
Ald6b	none	0	none	0	-6.38
Blank Calcite	none	0	none	0	-6.31
Ald4a	3% SAAC	1	none	0	-6.21
112196-4	3% SAAC	1	A2**	1	-6.39
112296-1	25% SAAC	1	none	0	-6.36
112296-1r	25% SAAC	1	none	0	-6.28
112296-2	25% SAAC	1	A2**	1	-6.56
112296-2r	25% SAAC	1	A2**	1	-6.39
112296-3	2.3% SAP	1	none	0	-6.24
112296-4	2.3% SAP	1	A2**	1	-6.47
3%IIIb1c	3% AEAPS	1	none	0	-6.35
110996-1	3% AEAPS	5	none	0	-6.41
110996-1r	3% AEAPS	5	none	0	-6.48
112096-2	3% AEAPS	5	A2**	1	-6.97
110996-2	25% AEAPS	1	none	0	-6.43
111096-1	25% AEAPS	5	none	0	-6.47
111096-1r	25% AEAPS	5	none	0	-6.46
111096-s	25% AEAPS	5	none	0	-6.39
110996-3	25% AEAPS	1	A2**	1	-7.42
111096-2	25% AEAPS	5	A2**	1	-7.32
111796-1	none	0	Conservare® H	1	-7.33
111996-1	none	0	Conservare® H	3	-7.20
112096-1	none	0	Conservare® H	5	-6.97
Ald8	none	0	Conservare® OH	1	-6.64

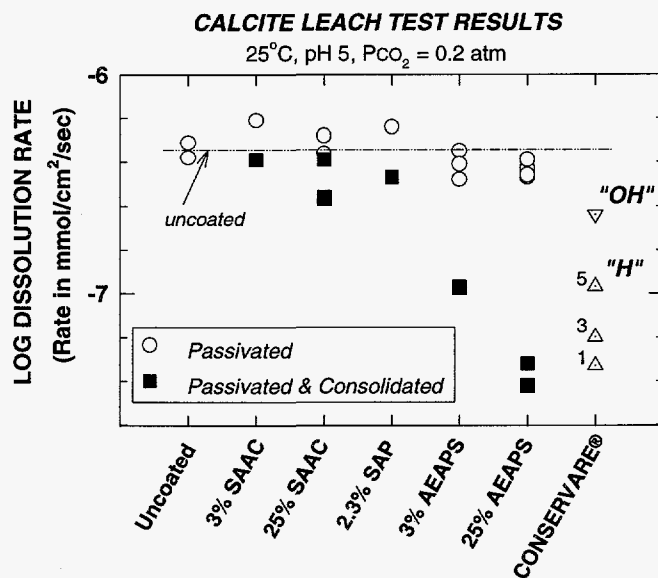


Figure 5. Dissolution rates of uncoated and coated calcite powders. All samples coated with passivants + consolidants yield slower dissolution rates than uncoated calcite. Numbers next to Conservare® data points represent number of applied coatings.

lated relative binding energies and packing configurations were used to develop a hierarchy of candidate passivant molecules and to explain dissolution rate data obtained in controlled pH-stat experiments. We have identified one passivant/consolidant combination: AEAPS plus A2** sol, that in short-term leaching tests works at least as well as the commercial product Conservare® H.

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