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Protective Coatings for Concrete

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PROTECTIVE COATINGS FOR CONCRETE

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ABSTRACT

The new two-layer protective coating developed for monuments constructed of limestone or marble was applied to highway cement and to tobermorite, a component of cement, and tested in batch dissolution tests. The goal was to determine the suitability of the protective coating in retarding the weathering rate of concrete construction. The two-layer coating consists of an inner layer of aminoethylaminopropylsilane (AEAPS) applied as a 25% solution in methanol and an outer layer of A2** sol-gel. In our previous work, this product when applied to calcite powders, had resulted in a lowering of the rate of dissolution by a factor of ten and was shown through molecular modeling to bind strongly to the calcite surface, but not too strongly so as to accelerate dissolution. Batch dissolution tests at 22°C of coated and uncoated tobermorite (1.1 nm phase) and powdered cement from Gibson Blvd. in Albuquerque indicated that the coating exhibits some protective behavior, at least on short time scales. However, the data suggest that the outer layer of sol-gel dissolves in the high-pH environment of the closed system of cement plus water. Calculated binding configuration and energy of AEAPS to the tobermorite surface suggests that AEAPS is well-suited as the inner layer binder for protecting tobermorite.

Methods and Results

Batch dissolution experiments were performed in which ~ 0.25 g of solid were added to ~ 125 mg of deionized water (initial pH ~ 6.5) in 125 mL PP bottles. The bottles were shaken periodically for about 22 hours. Three 10 mL solution samples were extracted using plastic syringes and 0.2 µm disposable filters, and analyzed for total dissolved Ca and Si using a SpectraSpan 7 direct-current argon plasma spectrometer. Two samples of uncoated tobermorite ($\text{Ca}_{4.5}\text{Si}_6\text{O}_{15}(\text{OH})_3 \cdot 2\text{H}_2\text{O}$) were reacted to assess experimental reproducibility. Powdered Portland cement from set and weathered road concrete was sieved for the < 100 µm fraction. The coating consisted of one layer of AEAPS (25% in methanol) and one layer of A2** sol-gel (Brinker et al., 1994). The samples and analyses are reported in Table 1.

Table 1: Experimental data. Si and Ca concentrations are in units of ppm. Tob. = tobermorite. Gib. = Portland cement from Gibson Blvd. in Albuquerque. The number after Gib. refers to cores obtained from the Pavement Materials Research Center of the Alliance for Transportation Research. Top refers to the top weathered core surface and bottom to a sample taken about 9 inches below the top surface.

	Tob. 1 uncoated	Tob. 2 uncoated	Tob. coated	Gib. 6 uncoated	Gib. 6 coated	Gib. 9 top uncoated	Gib. 9 top coated	Gib. 9 bottom uncoated	Gib. 9 bottom coated
1 hr Si/Ca	7.0/8.1	5.8/7.6	9.1/7.7	4.5/56.1	8.8/19.1	3.1/56.4	13.3/21.8	3.7/63.0	9.8/18.8
3 hr Si/Ca	11.2/10.0	9.2/9.0	13.0/8.0	4.3/63.0	11.2/21.3	3.2/60.8	18.2/25.8	3.6/67.8	13.4/22.1
22 hr Si/Ca	16.4/11.9	14.3/10.9	25.7/8.6	4.1/63.0	17.3/23.9	3.1/67.4	27.3/30.5	3.4/74.9	20.9/27.3
Final pH	9.88	9.94	9.81	11.75	10.72	11.77	10.58	11.83	10.66

In all samples, dissolved Ca was lower in the coated experiments by a factor of 0.25 to 0.75. The Ca released in the uncoated "set" cement experiments is similar to that released during hydration of Portland cement pastes (Goni et al., 1996), however, the pH is ~1.7 units lower. In contrast, dissolved Si increased for the coated samples by a factor of 1.5 to 9. The final pH of the tobermorite samples was about 10, while that of the cement samples was 11-12. In all cases, the final pH of the coated samples was slightly less than that of the uncoated samples.

The binding energy of AEAPS to the (001) surface of tobermorite was calculated by first energy-optimizing the AEAPS as a free gas phase molecule, and then docking it onto a molecular cluster representation of the fixed tobermorite structure. The binding energy was 165 kcal/mol. Further refinements of the calculation would be expected to change this by 25-30%. Compared to the calcite substrate, AEAPS appears to bind three times more strongly to tobermorite, although still much less strongly than other charged anionic passivants investigated in the previous study that actually contributed to increased calcite dissolution (Nagy et al., 1997).

Discussion and Conclusions

The calculation and experimental results on Ca release rates suggest that the two-layer protective coating holds some promise for sealing and protecting concretes. However, evaluation of the behavior of the alkoxysilane sol-gel itself in the high pH environments generated within hydrated concrete is necessary. Also, any secondary phase formation should be monitored closely in order to completely address the changes in chemistry observed. For example,

formation of calcite at the surface could be controlling the concentrations of Ca observed in the experiments. This process is known to occur at the surfaces of concretes and could be advantageous in that the protective coating has already been demonstrated to lower the dissolution rate of calcite (Nagy et al., 1997). Although the Si-release rate data indicated that the sol-gel may be unstable, longer-term experiments are needed to investigate the extent of dissolution of the sol-gel both at the high pHs found within cement and also at the pHs of concrete surfaces exposed directly to the environment. The latter also should be performed using a pH-stat apparatus to achieve pH values closer to neutral.

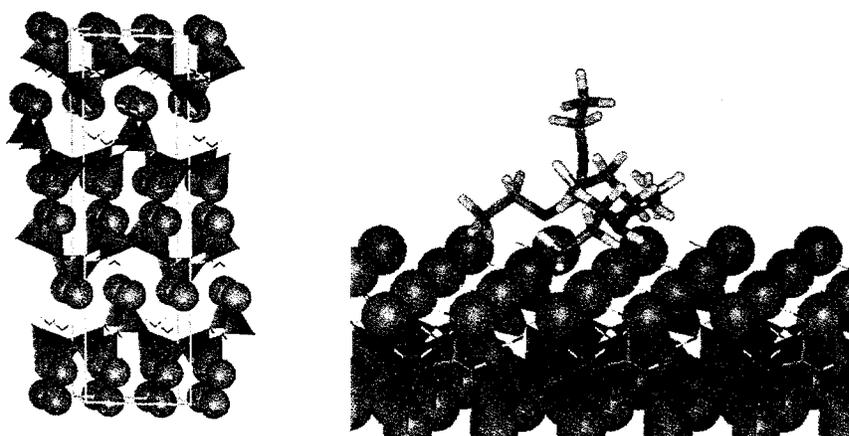


Figure 1: Image on left shows the tobermorite structure. It is monoclinic with infinite SiO_4 chains parallel to the b axis. Every third tetrahedra has two hydroxyls, and water molecules occur near the concave section of the silicate chain. The Ca ions are represented by the spheres and Si-tetrahedral units are represented as polyhedra. On the right is the energy-minimized docked position of AEAPS on the (001) surface near the Ca layer.

A workshop convened as part of this project involved participants from SNL, LANL, the Alliance for Transportation, the State of New Mexico, New Mexico Tech, Princeton, and the University of Illinois. Key issues in the area of concrete preservation were discussed and underscore the widespread concern over this topic. Our research plus the workshop discussions indicate large potential for future collaboration on research related to preserving concretes.

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