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A New Method for the Treatment of Iron-Stained Architectural Marble: *in situ* reduction of iron(III) using photovoltaic polymers and the introduction of a new chelating agent for conservation

Abstract

The problem of treating iron-stained marble is complex, especially when considering architectural marble that is subject to repeated iron deposition. Care must be taken to ensure that the marble matrix is not harmed during treatment. Theoretical conditions are considered, and a cleaning system is proposed that incorporates N, N, N', N'-tetrakis-(2-pyridylmethyl)ethylenediamene as a chelating agent and electrically conductive conjugated polymers capable of reducing deposited iron species. The proposed treatment system is evaluated using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). Directions for future research are suggested.

1. INTRODUCTION

From ancient to modern and contemporary, from West to East, from the sacred to the profane, marble surfaces are ubiquitous features of nearly every major city in the World in the form of sculpture, architectural facades, fountains, monuments, and the mundane. As future and current conservators, we are charged with the responsible care of these artifacts. As with any treatment, the cleaning of marble should strive to affect an aesthetically desirable surface while being minimally invasive.

The causes and mechanisms of marble deterioration are well known and documented.[1] In the interest of time, they will not be discussed in great detail here. However, it may be helpful to quickly outline these sources to illustrate the idea that the condition of a marble surface depends greatly on a number of interwoven factors. One could easily categorize any cause of deterioration of exposed marble surfaces into four major groups: chemical, environmental, biological, or man-made. Several factors leading to the deterioration of marble surfaces could easily fall into more than one group; acid rain, for example, can be seen as resulting from man-made pollution, wet and dry atmospheric deposition and subsequent chemical degradation. The development of iron staining on marble surfaces also falls into multiple categories in that the iron source is usually the result of human design and the iron is transported to the surface by rain or fountain water.

A real-life example of a staining problem, and the impetus for much of this research in the grand fountain at Nemours, the site of a former 300-acre estate of Alfred I. duPont (Figure 1). The fountains are part of the Louis XVI-style garden on the estate just outside of Wilmington, Delaware. Several marble and other stone sculptures and architectural structures are placed throughout the gardens. At the time of this writing, Nemours has embarked upon a two million dollar restoration project that includes the cleaning of the

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[1] A quick literature search yields varied resources on marble deterioration. See Carfagni (2003), Spurny (2000), Richardson (2001), and St. Clair and Seaward (2004), for example.

marble fountains, which have been in use since 1911. The original plan was to use commercially available stone cleaning preparations to remove the staining with the intent of returning the fountains to working order soon thereafter.

Figure 1: Iron-stained marble fountains at Nemours

2. PREVIOUS APPROACHES TO CLEANING

The problem of removing iron staining satisfactorily, efficiently, and safely has historically proven to be challenging. Looking through a sampling of the conservation literature, one sees a wide range of reagents and pHs used (See Table 1). The majority of published studies follow one or both of two main themes: acidic preparations and the use of strong chelators. In addition, many of the solutions shown here also included high ionic content as part of the driving force to remove the staining. The result of all of these conditions is the removal of iron staining by undercutting the stain – that is, attacking the marble rather than the stain.

Table 1: Some Conservation Preparations for Cleaning Iron-Stained Marble

Reagent	pH	Reference
AB 57	10	Mora et al. 1984
Ammonium Thioglycolate	8	Windholz 1983
Ammonium Thiosulphate	*	Stambolov and van Rheeden 1968
Citric Acid	3	MacLeod and North 1979, MacLeod 1987
EDTA	4	Alessandrini et al. 1984, Thorn 1993
EDTA	11	Thorn 1993
Sodium Thiosulphate	*	Stambolov and van Rheeden 1969
Sodium Gluconate	6	Stambolov and van Rheeden 1968, Edos 1990
Sodium Hydrosulfite	9	Merk 1981, Gilberg 1982, Barov 1987
Thioglycolic Acid	*	Stambolov 1968, Edos 1990, Howie 1974
Ammonium Citrate	9	Matero and Tagle, 1995
Ammonium Citrate	6.5	Gale 1982
“Bio-Pack” and Hydrofluoric Acid	2.5	Sramek 1991
Versenol (EDTA)	*	Plenderleith 1955
Oxalic Acid, Citrate, and EDTA	*	Rinne 1976
Trisodium Citrate	8	Stambolov and van Rheeden 1968

The same problem exists in industrial applications as well. Although commercial products have been formulated specifically for the cleaning of marble and other carbonate surfaces, there are very few if any products deemed safe that are specifically designed for the removal of iron staining. If one were to clean the marble surfaces of the fountain with these materials and allow thousands of gallons of water to be cycled over the surface, would we be dooming the fountain, whose surfaces remain in a fragile, sugary state after having been cleaned repeatedly over the years and exposed to the elements, to a harmful and expensive cycle of cleaning and staining?

This begs the question - is it possible to define theoretical parameters for a cleaning system that will efficiently remove iron staining without disrupting the marble matrix?

3. DESIGNING AN APPROPRIATE CLEANING SYSTEM

There are three main issues that need to be addressed in the formulation of a suitable cleaning solution. Maintaining an appropriate pH is of great importance in achieving the goal of harming the marble substrate as little as possible. Likewise, appropriate use of chelating materials is important. The goal here is to manage the insoluble iron and begin to bring that insoluble material into solution without breaking apart the marble matrix. Finally, the ionic strength of a solution must be considered.

3.1 pH Considerations

Marble is a considerably complex and diverse material made up of several different carbonates, oxides, hydroxides, and silicates. The primary component, however, is Calcium carbonate, typically calcite. Aside from the simple fact that one should probably not drift too far from a pH equal to calcite's pK_a of 10.33, another factor in the dissolution of calcite should be considered as well. The chemistry of carbonate stones is such that when in contact with water, the dissociation of calcite is driven by two factors: pH and the partial pressure of carbon dioxide in solution.[2] If one were to bring an acidic preparation to a marble surface, the relatively high hydronium ion concentration would drive the dissolution of the marble toward completion. Likewise, dissolution would be favored in an arrangement where carbon dioxide is cut off from the surface, all things being equal.

$$CaCO_3 \rightleftarrows Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \rightleftarrows HCO_3^- + OH^-$$

$$\underline{H^+} + HCO_3^- \rightleftarrows H_2O + \underline{CO_2}(g)$$

The consequence of this relation is that if we bring a thin film of cleaning solution to a surface, where the partial pressure of CO_2 in solution is roughly equal to that of atmospheric concentrations, the dissolution of the calcite is favored at a pH below about 8.3. However, if a poultice or a gelled preparation is used to clean the surface, the partial pressure of CO_2 at that surface is reduced. As the partial pressure of CO_2 decreases, the

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[2] For a discussion of chemical considerations in marble cleaning applications, see Livingston (1992).

amount of calcium going into solution reaches a minimum around a pH of 10 (Figure 2). Since using a poultice or gel is probably unavoidable in these situations, working at a pH near 10 should help to minimize the amount of damage possible to the marble surface.

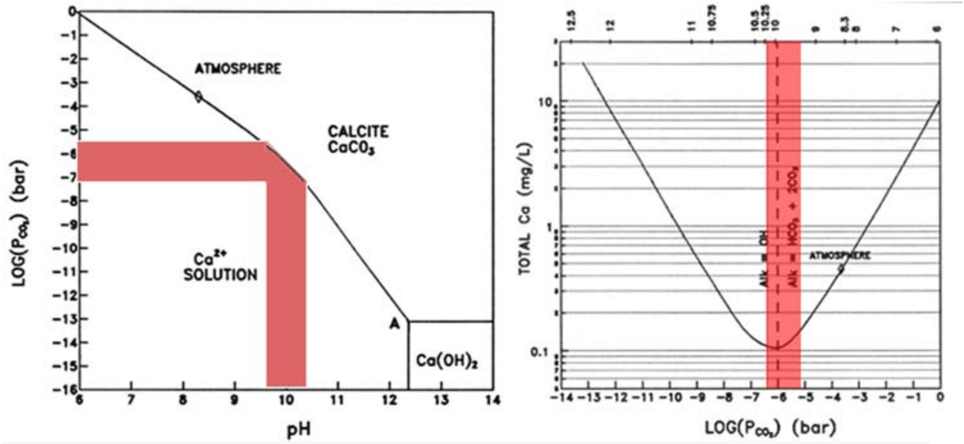


Figure 2a (left): Calcite saturation as a function of pH and P_{CO2}
Figure 2b (right): Calcite saturation vs. CO_2 pressure
The highlighted regions represent conditions of minimum solubility at decreased carbon dioxide concentration. Figures adapted from Livingston (1992).

3.2 Chelating Materials

The use of a chelating agent to complex and help remove staining materials is the next factor that will be considered here. While calcium carbonate and other compounds found in and on marble surfaces are relatively insoluble materials by themselves in water, they can begin to be broken up and brought into solution by the introduction of chelating materials. A convenient way to consider the relative strength of a chelating material is to compare its formation constants for the metal ions of various species to the solubility product of those species (Table 2). In general, complexation is favored when the formation constant of the complex is greater than the solubility product constant of a given material. The goal, then, is to select chelators that will disassemble iron species and not the marble itself.

Table 2: Solubility Product and Formation Constants for Common Species and Chelators

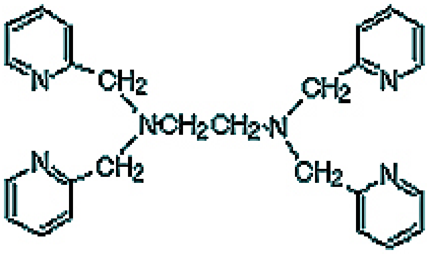
	pK_{sp}*	K_f, Citrate	K_f, EDTA	K_f, NTA	K_f, Oxylate
Ca^{2+}	8.35	4.68	11.0	7.6	3.0
Fe^{2+}	14.43	3.08	14.33	8.84	5.22
Fe^{3+}	37.4	12.5	24.23	15.87	9.4

***pK_{sp} values correspond to prevalent species in the marble matrix and in the iron staining.**
Data from CRC Handbook.

Examining formation constants for a few of the more commonly used chelating materials and solubility product constants for bulk materials in marble, a few points of interest arise. First, it is clear that EDTA is far too strong a chelator to use for this application, as calcium will be taken up and brought into solution. And while some chelators like citrate and oxalate should be safe for the marble surface, none of these materials, EDTA included, should be able to efficiently bind the iron species. It should be apparent by looking at these numbers that bringing a strong chelator like EDTA to an iron-stained marble surface will never serve to solubilize the iron staining – instead, the stain would be removed by attacking the marble surface and undercutting, thereby damaging the surface, albeit microscopically. However, repeated cleanings over hundreds of years combined with environmental exposure would leave a surface far removed from the original. Iron(II) complexes, with formation constants on the order of 14, are far more manageable than iron(III). However, this presents two problems: selecting a suitable chelator, and finding a way to efficiently reduce iron(III) to iron(II).

3.2.1 TPEN: N, N, N’, N’-tetrakis-(2-pyridylmethyl)ethylenediamene

Looking to other fields, one might be able to find materials suitable for conservation that offer greater specificity than some of the more traditional materials can allow. One promising example is TPEN, N,N,N’,N’-tetrakis-(2-pyridylmethyl) ethylenediamine (Figure 3). In applications where biologically active trace concentrations of calcium are monitored in cell structures using fluorescent dyes, the fluorescent dyes also bind to heavier metals such as copper, zinc, manganese, and iron, making detection difficult. TPEN, however, binds strongly to those heavier metals and does not bind well to calcium and magnesium. TPEN, then, is used to mask heavier metals by preventing the fluorescent dyes from binding with them.[3]



<u>N,N,N’,N’-tetrakis-(2-pyridylmethyl)ethylenediamene</u>

- Water soluble
- $pK_a^1 = 10.27$
- K_f, $Ca^{2+} = 4.4$
- K_f, $Fe^{2+} = 14.61$
- High affinity for heavy metals
- Also binds weakly to magnesium

Figure 3: TPEN and its properties as a chelator

Several properties of TPEN are convenient and novel for the current problem. TPEN is water-soluble. The first pK_a of TPEN is 10.27, very close to the pK_a of calcite and our operating pH of 10. TPEN also has a formation constant for iron(II) higher than that of EDTA, and a formation constant for calcium lower than citrate. TPEN’s formation constant for calcium is lower than calcite’s pK_{sp} and the formation constant with iron(II) is almost equal to the pK_{sp} of iron(II) hydroxide. This suggests that TPEN should be able to dismantle some iron(II) species without harming the marble matrix.

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[3] See Hofer (2001).

3.3 Managing Iron(III) Using Conjugated Polymers

Looking at a Pourbaix diagram showing the relationship between speciation, pH, and electrical potential for an iron-water system, it is possible to see how insoluble iron(III) can be reduced to iron(II) (Figure 4). For a solution at a pH of 10 with an oxidation-reduction potential of zero millivolts, the dominant form of iron shown here is Fe_2O_3. Given the pH range determined before, if one can get close to providing a reducing potential of 300 to 400 millivolts, we will begin to reduce some of the iron(III) to iron(II). This, of course, does not mean that we should begin hooking batteries up to our marble objects. A more elegant and reasonable solution would be to include materials capable of creating a reducing potential in the cleaning system.

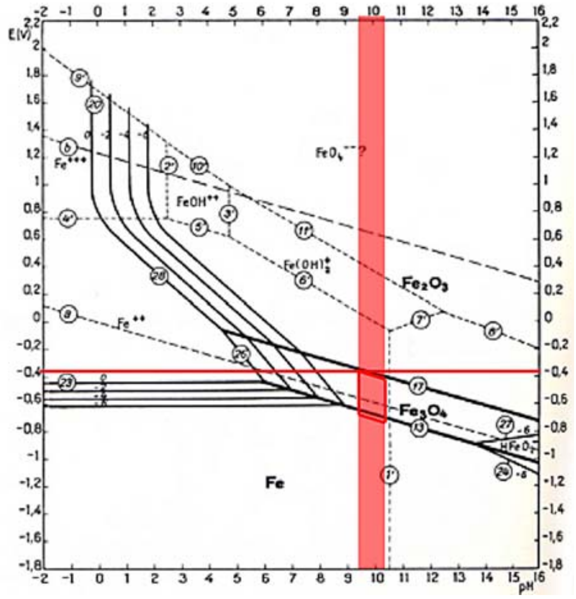

Figure 4: Pourbaix diagram for an iron-water system. The highlighted region denotes the pH range determined before, and the horizontal line at around -400mV marks the point at which formation of iron(II) species is favored.

Conjugated polymers are a fairly recent development, with the discovery in 1977 that certain plastics could be made conductive. Conventional wisdom would suggest that polymers and plastics are insulating materials. Yet, within the past five or so years since becoming commercially available, conjugated polymers have been incorporated into organic LEDs, anti-static coatings and films for electronics, and even as corrosion inhibitors in some commercial metal primers.[4]

The conjugated polymer being proposed for use here is a water-soluble sulfonated polyaniline[5]. The conducting nature of the polymer arises from the repeating stretches of alternating single and double bonds, as well as sulfate groups and amine groups that result in a large mass of delocalized electrons, not unlike that in a metal or semiconductor. Most conjugated polymers absorb heavily in the visible and ultraviolet regions of the spectrum and the promotion and replacement of electrons in the delocalized field allows the polyaniline to conduct and transfer electrons.

A novel approach is to pair different conjugated polymers together to increase efficiency. A water-soluble polythiophene, sodium poly[2-(3-thienyl)ethoxy-4-butylsulfonate], acts a photovoltaic polymer. In a basic solution like the one proposed here, the polythiophene absorbs heavily in the blue and green regions of the visible spectrum as well as in the UV. Conveniently, the resulting fluorescence maximum is very close to one of the

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[4] For extensive discussions on electrical characteristics and industrial applications of conjugated polymers, see Salaneck, et al. (1996) and Rupprecht (1999).

[5] ADS650WP available from American Dye Source, Inc. http://www.adsdyes.com

absorption maxima of the polyaniline at 566 nm. The polythiophene, then, acts to harness the light energy and feed energy to the polyaniline, increasing the amount of energy transferred by the polyaniline.

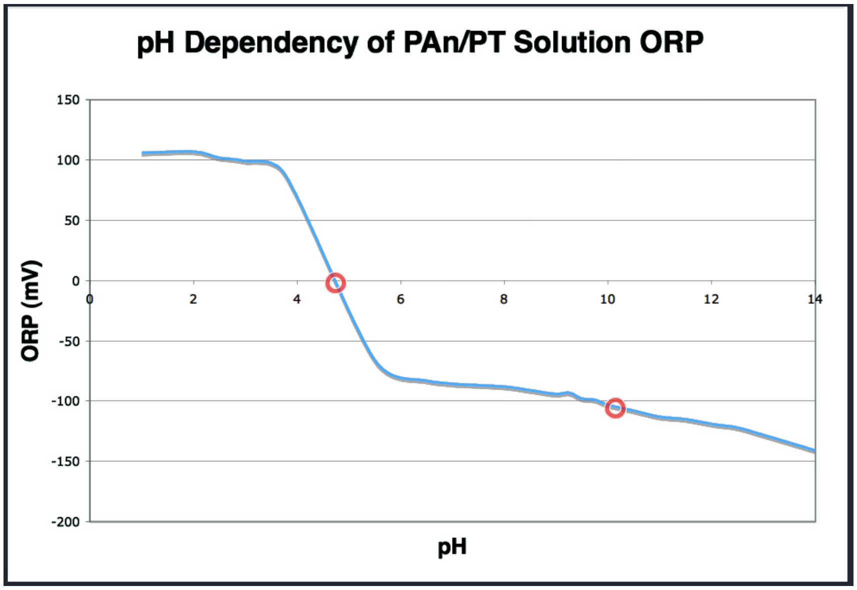

Figure 5: pH dependency of PAn/PT Solution ORP.

The plot in Figure 5 shows the pH dependency of a polyaniline and polythiophene solution's oxidation-reduction potential. Around pH 5, the solution changes from an oxidating potential to a reducing potential. Also of note is that around a pH of 10, the potential begins to decrease more rapidly. While the ORP of this test solution reached between 100 and 150 millivolts of reducing potential, in final preparations and under UV light as in outdoor conditions on a sunny day, a reducing potential of around 270 millivolts was achieved. While this is shy of the desired value of near 400 millivolts of reducing potential, it should create a condition where some of the available iron(III) would be reduced to iron(II).

3.4 Ionic Strength Considerations

Now that two of the major factors have been considered, it is important to make at least a quick note about the ionic strength of the cleaning solution. The main point to take away here is that having a high ionic content to the cleaning solution creates a large pressure for that ionic material to move into and disrupt the surface of the stone. Another important point is that bringing a large amount of salts to a stone surface increases the chance for salts to diffuse deep into the surface and potentially cause damage upon recrystallization. It would be advantageous, then, to not include a high salt concentration in the cleaning solution if the goal is to not disrupt the stone surface.

While it is true that the conjugated polymers impart a high conductivity to the cleaning solution, it is important to remember that these are high molecular weight polymeric materials that cannot diffuse far into a stone surface, especially in a gelled preparation.

3.5 Cleaning Formulation

Here is a look at the final cleaning formulation. Again, we will be working with an aqueous system as we are dealing with inorganic, ionic materials for the most part here. The conjugated polymers are included to reduce the iron and make it more manageable. TPEN is used as a chelating material to remove iron staining and other salts on the surface. Sodium carbonate is added to set up a carbonate-bicarbonate buffer system to maintain a pH around 10. Finally, Vanzan, a pharmaceutical grade xanthan gum is added as a gelling agent.

100 mL Deionized Water
1 mg Polyaniline & Polythiophene
1 g TPEN
Sodium Carbonate added to adjust pH to 10
1 g Vanzan

4. TEST CLEANING

In testing the cleaning solution, it became clear that the ability to remove staining depended greatly upon the availability of iron and the depth of stain penetration. Where iron is readily available close to the surface, the cleaning system works very well and efficiently, taking on the order of only 1 to 2 minutes for stain removal (Figure 6). The cleaning formulation allows some degree of "tuning" in that a number of variables can be manipulated to achieve the desired effect. Chelator and polymer concentration, duration of application, and exposure to light can all be easily adjusted.

Figure 6: A test cleaning after approximately two minutes of gel application.

Remember that some of these surfaces have been stained for several years and there has been sufficient opportunity for the staining to become deeply entrenched in the marble surface. For very deep stains, the cleaning ability of the solution was slight but noticeable, which is reassuring in that the cleaning preparation is not undercutting deep into the marble surface.

Stained samples of marble were examined before and after cleaning using SEM-EDS (Figure 7). The important features to note here are the differences in the peak height ratios of calcium and iron between the uncleaned and cleaned areas. It is also important to note that the surfaces do not appear to be too morphologically dissimilar in the secondary electron images.

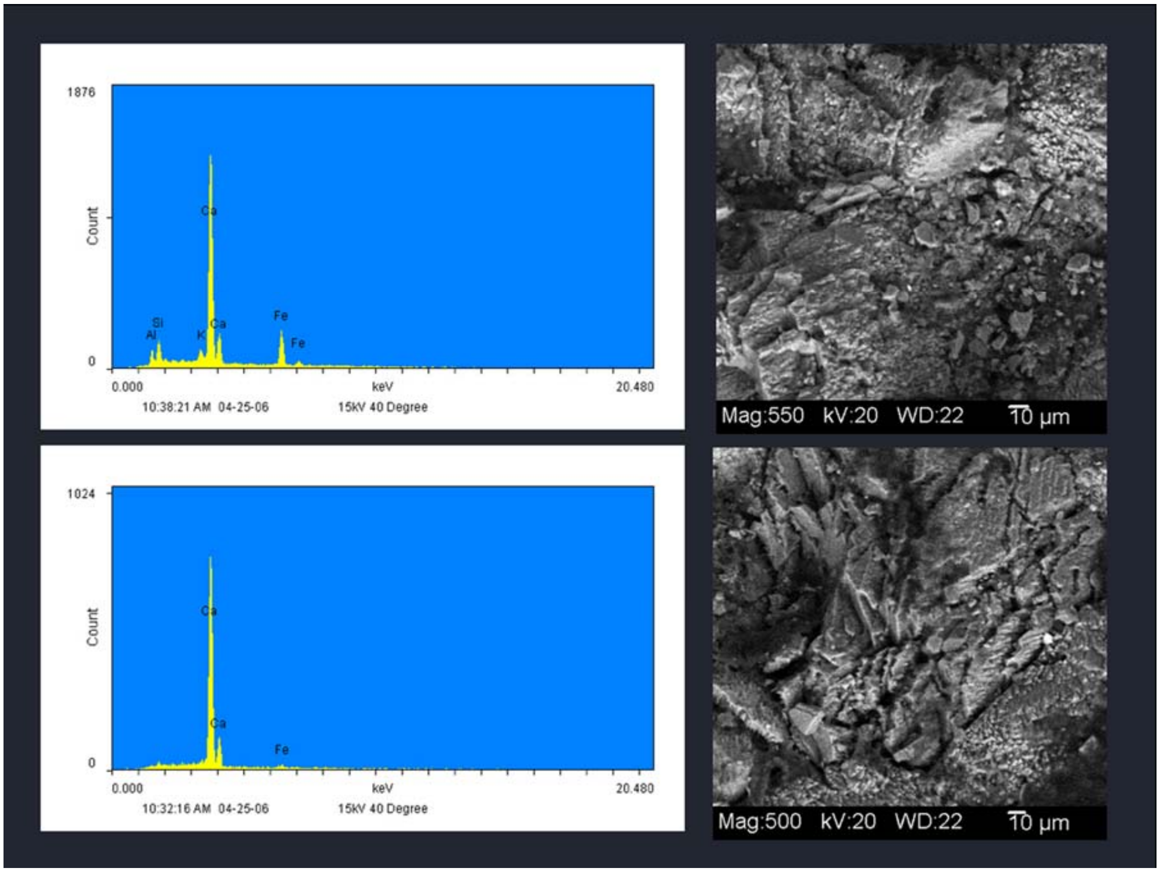

Figure 7: SEM-EDS spectra and secondary electron images for uncleaned (top) and cleaned (bottom) areas of an iron-stained architectural marble fragment.

5. CONCLUSIONS AND FUTURE RESEARCH

The proposed cleaning system has illustrated possible uses for recently developed materials from research and industry in conservation applications. Preliminary testing suggests that the cleaning system is capable of reducing and chelating iron species while causing minimal damage to the marble surface. Continued research in several areas may help to address related problems and refine the problem at hand.

5.1 Toward a Water-Reversible Conductive Coating

While the proposed cleaning system is promising, the problem of repeated iron deposition as a result of nearby metal elements, or from cycled water in the case of fountains, needs to be addressed. To that end, attempts have been made toward creating a coating system that would prevent the marble from becoming stained. This coating would act as a retreatable maintenance coating that ideally would be able to stand up to complete immersion in water over long periods of time. In the interest of brevity, the development and testing of this coating will not be discussed in full here.

However, the desired characteristics of the coating are many and can be discussed briefly. Ideally, the coating should be insoluble in normal rain or fountain water – that is, neutral and acidic pH. Yet, because this would be in an outdoor setting, it might be more environmentally sound and safe for the coating to be reversible in alkaline pHs rather than in organic solvents. For the same reasons, it would be desirable to deliver the coating in a water or alcohol solution. The inclusion of materials capable of producing a reducing potential would be advantageous in that iron would be less likely to settle into the stone as an insoluble material. The coating would also have some anti-static properties in this case that could prevent the deposition of small particulates. Obviously, the coating would need to be stable in a wide range of environmental conditions. And last, but certainly not least, the coating would need to be aesthetically neutral – that is optically clear, not too glossy, etc.

What has been proposed so far is to base the coating on Avalure AC315, a lightly cross-linked poly acrylic acid, which is used in the cosmetics industry for applications such as nail polish that can be removed at relatively high pH (around 10 or 11). As with the cleaning system, polyaniline and polythiophene would be included. And, taking a page out of library and paper conservation, including an alkaline reserve such as Wei-T’OH or some carbonate salts, would serve to maintain the pH of the coating near the equilibrium pH for calcite at reduced CO_2 concentration. The alkaline reserve would also serve as cross-linking agent, allowing the coating greater stability in water. However, more testing needs to be conducted.

5.2 Other Avenues for Future Research

Understanding the cleaning problem at hand would be aided greatly by conducting in-depth comparative studies of marble cleaning preparations and techniques, both past and present. Looking to related fields for selective chelating agents would be advantageous as these materials are being developed in large numbers for specialized applications. Along the same lines, more efficient and longer lasting conjugated polymers and other conductive materials should be pursued and considered. Lastly, it may be useful to examine the benefits of incorporating conductive into conservation coatings.

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