Cleaning Marble with Ammonium Citrate

Claire Gervais, Carol A. Grissom, Nicole Little and Melvin J. Wachowiak

Ammonium citrate solutions were tested to determine possible damage on marble using two concentrations, four different values of pH and several variations in application. As pH dropped from values of 10 to 7, marble chips immersed in the solutions showed increasing dissolution of calcite, and polished marble tiles to which solutions had been applied showed increasing loss of gloss and brightness. The least damage to marble tiles was produced when solutions were covered during application, and single cleanings were found to be less damaging than multiple cleanings of the same total application time. Comparison with other cleaning agents – ammonium thioglycolate and ethylenediaminetetraacetic acid (EDTA) – showed that ammonium citrate solutions could be as mild as thioglycolate when used in some conditions, such as high pH and low concentration. In contrast, ammonium citrate solutions could harm the stone significantly when used in other conditions, such as pH 7 or high airflow. In these cases, the damage was nearly as much as a 2% solution of EDTA at pH 10. This study emphasizes the need to develop new cleaning products, research which can only go hand in hand with a better understanding of the various interactions taking place between cleaning agent, substrate and environment.

INTRODUCTION

The cleaning of stone monuments, statues or facades may be performed for a variety of reasons. It is probably most often undertaken for aesthetic reasons, but may also be done when soiling actively contributes to the deterioration of stone [1]. Selecting the appropriate cleaning method is a delicate matter. Factors such as type of stone, degree of deterioration and type of soiling must be taken into account [2, 3]. An understanding of the mechanisms of the cleaning process and the potential interaction of the cleaning product with the stone are also fundamental to the choice of a safe cleaning product. This study focuses on ammonium citrate and its potential impact on marble surfaces, for which no systematic investigation has been done.

The ecological and human harmlessness of citric acid and its salts plays a role in its widespread use as a cleaning agent [4]. In the conservation field, citric acid was reported to be effective for removal of iron corrosion products nearly 40 years ago [5], and its ammonium salts have been advocated over the past 20 years as mild but efficient cleaning agents for removing soiling from both varnished and unvarnished paintings [6]. The popularity of ammonium citrate for cleaning stone artifacts or monuments is fairly recent. Publications have reported on the removal of two types of stains: soiling that was hard to remove by other methods from limestone Egyptian statues [7] and French eighteenth-century marble medallions [8], and iron stains on the Metropolitan Club building in New York [9] and a Temple of Love on Long Island [10]. In practice, ammonium citrate solutions are now most widely used for routine removal of soiling from stone, and it is this use that is our principal interest. A solution of ammonium citrate 5% (w/v) buffered to pH 9 with ammonium hydroxide seems to be the most common formula.

Little explanation of ammonium citrate's action on stone is found in the literature. Results of careful studies on paintings to determine its mode of action on soiling, its effect on varnish and its potential harmfulness to the pigmented layer are partially transferable to the cleaning of stone, since the mode of action on dirt is likely to

Received August 2009

be the same [11–14]. However, the painting studies necessarily do not illuminate ammonium citrate's impact on stone. Ammonium citrate is known to chelate Ca^{2+} ions, for instance, which makes its use subject to caution on calcareous stone such as marble or limestone.

This study investigates the effect of ammonium citrate solutions principally on clean polished marble tiles to better understand its action on the marble matrix and establish the safest conditions for utilization. Since citrate chelates calcium ions, the solubility and rate of dissolution of calcite is established at different values of pH and concentrations of ammonium citrate. The impact on marble surfaces is monitored principally by measuring specular gloss on polished marble tiles before and after application of the cleaning solution.

Ammonium citrate as a cleaning agent

The efficiency of ammonium citrate (hereafter AC) as a cleaning agent is often associated with its chelating properties, i.e. the capacity of citrate to associate with various metals and form stable complexes, often soluble in water. The formation constants K_f of principal metal-citrate complexes follow the order Cu(II) > Fe(III) > Al(III) > Pb(II) > Zn(II) > Ni(II) > Co(II) > Cd(II) > Mn(II) > Mg(II) > Ca(II) > Fe(II) > Sr(II) > Ba(II) [14]. K_f values of citrate with Fe(III), Ca(II) and Fe(II) are 12.5, 4.7 and 3.1 respectively [15]. A significant discrepancy in these values is found in the literature, partly because measurements are dependent on temperature and ionic strength, which makes comparisons difficult. In addition, studies to determine the number, structure and domain of stability of metal-citrate complexes are ongoing. At least five different Fe(III)-citrate complexes have been recently characterized, for instance, but their behavior in solution remains unclear and is poorly documented [16]. In any case, it is clear that Fe(III) is readily complexed by citrate ions, and this at least partially explains AC's success in removing soiling, which generally contains iron, as well as iron stains. The formation constant for Ca(II) indicates that calcium-citrate complexes can also form, however, which means that citrate ions could attack calcareous stones such as marble or limestone by bringing calcium into solution. Indeed, several experts have attributed the apparent removal of soiling mainly to the dissolution of calcite when ammonium citrate is used [15, 17].

The ability of AC to remove surface dirt deposits cannot be explained exclusively by chelation, however, since many types of soiling are composed of organic substances, such as fatty acids from diesel fumes or oil combustion. Rather, the success of AC apparently stems from the complex and still not well-understood interplay among multiple properties. AC also acts as a surfactant, wetting agent and deflocculant [13]; this last function helps disperse and maintain particles in suspension, in particular by increasing the electrostatic repulsion of dirt particles between themselves and the surface. Citrate's counter-ion, ammonium, also seems to play a role in the cleaning process, probably explaining a difference in efficiency between sodium and ammonium. Indeed, the ammonium ion is known to be itself a good chelating agent (for instance, for copper) and wetting agent, and it may react with carbonyl groups in fats, oils, proteins and resins [14].

EXPERIMENTAL

AC solutions at different concentrations and pH values were prepared and used in a series of experiments, summarized as follows:

- Measurement of the dissolution rate and solubility of marble chips by inductively coupled plasma–mass spectrometry (ICP–MS). The solubility value (amount of calcium in solution at equilibrium) will indicate the maximum amount of marble that can be dissolved, while graphs showing dissolution rates over time will give an idea of application times that would minimize damage. This experiment is not representative of what could happen during cleaning, since the marble chips are totally immersed in cleaning solutions for a long period of time. However, it gives an idea of the absolute harmfulness of AC solutions independent of the mode of application, such as poulticing, swabbing, etc.
- Measurements of changes on polished marble tiles after application of a range of AC solutions by means of a glossmeter and microscope [18]. Polished marble is smoother than stone that requires cleaning, but it allows assessment of surface damage independent of weathering and inhomogeneity. Two other cleaning agents were also tested to provide a relative scale for comparison with AC: disodium ethylenediaminetetraacetic acid (EDTA) and ammonium thioglycolate, which have opposite effects on calcareous stone. Studies have shown that EDTA, used most often in the cleaning mixture AB57 – made of sodium bicarbonate, ammonium bicarbonate, disodium EDTA, Desogen (a surfactant), salt of quaternary ammonium and carboxymethylcellulose – is damaging to calcareous stone [19, 20], although it is

still used to some extent, especially on stone mosaics [21]. At the other end of the spectrum, ammonium thioglycolate, which has been used recently with success in removing iron stains, seems to be one of the safest cleaners for calcareous stone, particularly on marble [20]. Finally, the impact of the mode of application of the solution was tested to determine the influence of factors such as airflow and frequency of application.

Preparation of cleaning solutions

A total of eight solutions of AC were prepared at concentrations of 2% and 5% (w/v) adjusted with ammonium hydroxide to pH values of 7, 8, 9 and 10. Since the evaporation of ammonium ions in the form of ammonia (NH_3) is known to significantly change the pH of solutions, bulk solutions were covered with Parafilm throughout the experiment. Before each use, the pH was measured with a Fisher Scientific Accumet AB15 pH meter and adjusted with drops of ammonium hydroxide as necessary. All solutions were prepared with deionized (DI) water.

Triammonium citrate (pH ≈ 7.0) was used for preparing the AC solutions. AC solutions could also have been prepared starting with diammonium citrate (pH ≈ 4.3) and would have resulted in the same final products, but that would have required much more ammonium hydroxide to adjust the solutions to desired pH levels. Figure 1 demonstrates the distribution of ammonium and citrate ions by pH. The primary difference between di- and tri-ammonium citrate lies in the distribution of the salt (i.e. position) along the pH curve, and therefore the number of ammonium ions present in the salt form. In solutions of greater than pH 8 the citrate is completely ionized, and three NH_4 groups are needed, either initially added with the salt using triammonium citrate or using diammonium citrate and adjusting the pH with NH_4OH. Note that adjusting the pH with another base such as sodium hydroxide would not form triammonium citrate, but rather diammonium sodium citrate. Three comparative solutions were prepared as follows. Disodium EDTA 2% (w/v) was adjusted with sodium hydroxide to pH 7 and pH 10, and ammonium thioglycolate 5% (w/v) was adjusted with ammonium hydroxide to pH 9.

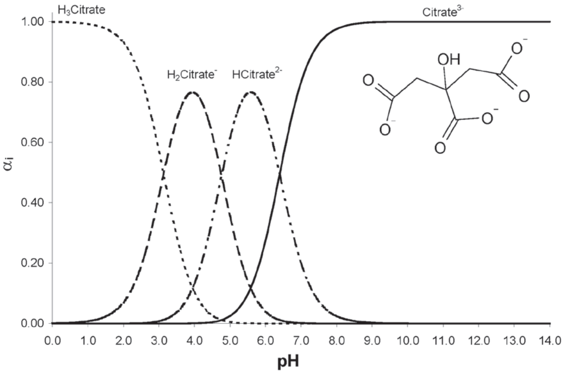

Figure 1 *Distribution of citrate ions as a function of pH, computed by Curtipot [22]. Values for pKa are 3.13, 4.76 and 6.40 respectively.*

Solubility measurements of marble chips by ICP-MS

Twenty grams of unpolished marble pebbles, similar in shape and size (c. 50 × 80 × 2 mm), were immersed in 150 mL of each of the eight AC solutions in 250 mL beakers at room temperature (c. 20°C). Homogenization was ensured by gentle magnetic stirring. Care was taken in the consistency of the experimental set-up because of the dependence of the solubility of $CaCO_3$ on variations in temperature, volume, etc. [23].

Approximately 2 mL of each solution were extracted at regular intervals and analyzed by ICP-MS to determine the amount of calcium dissolved (see Appendix). Removal of solutions did not affect results, since varying the number of extractions did not result in different solubility curves (results not shown). Cotton filters at the tips of Pasteur pipettes prevented tiny particles of marble that could alter measurements from entering the extractions. The monitoring period was 62 hours, and reproducibility was verified by repeating the experiment that used 5% AC at pH 9.

Gloss measurements on marble tiles cleaned in three series of experiments

White Carrara marble tiles (30.5 × 30.5 × 1 cm) were divided into nine squares measuring 10 × 10 cm each. Solutions were pipetted onto test areas instead of using a poultice, because a poultice would have introduced heterogeneity into the contact between the cleaning solution and surface, leading to problems of reproducibility. Moreover, results would depend on the type of poultice (porosity and content), the ratio of the poultice to the solution and the actual contact area between the cleaning solution and marble surface, rendering comparisons difficult. Rinsing was performed with $CaCO_3$-saturated water, prepared as described in the Appendix. $CaCO_3$-saturated water was used to rinse surfaces rather than DI water, since DI water contains almost no ions and tends to strongly solubilize calcium ions, thus etching marble [24]. A simple test was conducted consisting of immersing polished marble tiles for 20 minutes in DI water and $CaCO_3$-saturated water. The tile immersed in DI water had clear visual etching of the surface, whereas none was observed on the tile immersed in $CaCO_3$-saturated water.

In a first series of cleaning tests, each of the eight AC solutions was systematically applied to fully cover its square using two full pipettes of AC solution (c. 3 mL total). Care was taken to keep the surface covered with solution and avoid swabbing. After four minutes, excess solution was removed with paper cleaning tissue; the surface was immediately rinsed with $CaCO_3$-saturated water wiped over the surface for 30 seconds with cotton wool. The rinsing process was repeated a second time, and the entire procedure was performed twice for each AC solution.

In a second series, the mode of application of the cleaning solution was investigated by applying a solution of 5% AC (w/v) at pH 10 to a marble tile for four minutes in four different ways. The solution was applied: (1) for four minutes in open air (same protocol as in the previous experiment); (2) for four minutes in a laboratory fume hood with air extraction set on maximum; (3) for four minutes with the solution covered with Parafilm; and (4) for one minute followed by two 30-second rinses, repeated four times to give a total of four minutes' cleaning. Each procedure was performed four times.

In a third series, two other cleaning agents were applied for comparison to AC solutions. Using the same protocol as the first series, these solutions consisted of disodium EDTA 2% (w/v) at pH 7 and 10, and ammonium thioglycolate 5% (w/v) at pH 9. Because of the strong odor and harmfulness of thioglycolic acid to humans, this product was applied in the fume hood with medium air extraction.

Specular gloss measurements on test areas were made using a glossmeter according to the method described in the Appendix. Computation of the average normalized gloss difference ΔG_{norm} between areas measured before and after cleaning is also described in that section.

Reflected bright-field microscopy on a marble tile

On part of a marble tile small enough to be placed under a microscope, 25 test areas of approximately 1 cm square were defined. Twelve cleaning solutions were applied to two squares each, randomly chosen; one square was left blank as a control. Solutions included the eight AC solutions, EDTA 2% (w/v) at pH 7 and pH 10, ammonium thioglycolate 5% (w/v) at pH 9, and DI water. A drop of solution was applied on the test area and left untouched for four minutes. The drop was then removed with a paper cleaning tissue, and the surface was rinsed with $CaCO_3$-saturated water. Microscopic analysis was performed according to the protocol described in the Appendix.

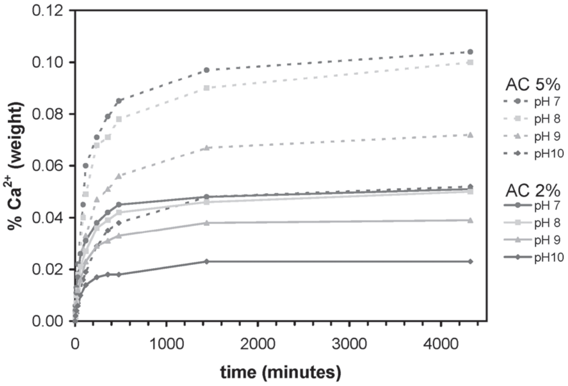

Figure 2 Dissolution rate of calcite for marble chips, expressed as calcium ion concentration in two different AC solution concentrations at four pH values each. Calcium ion concentrations were measured by ICP-MS.

RESULTS AND DISCUSSION

Dissolution rate and solubility of marble chips in various AC solutions

Dissolution rates of marble chips in 2% and 5% (w/v) solutions of AC at four pH values are shown in Figure 2. The dissolution curves are similar in shape, with sharp increases during the first hour during which approximately half of the Ca^{2+} was dissolved; this is followed by slowing dissolution and convergence toward plateaus. Since the rate of dissolution increases so sharply at the beginning, this suggests that repeated applications may produce more damage, as was confirmed in a subsequent experiment on marble tiles. The final value corresponds to the thermodynamic solubility of calcium ions, i.e., the maximum amount of Ca^{2+} that each AC solution can dissolve in these conditions of temperature and pressure.

For better comparison, solubility taken as the percentage of Ca^{2+} in solution after 4320 minutes (72 hours) is plotted against pH in Figure 3. Clearly, both concentration and pH play roles in the dissolution process, and three main observations can be drawn:

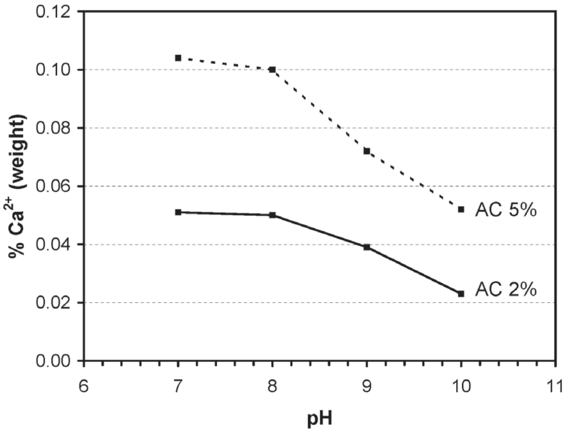

Figure 3 Solubility of calcium ions for marble chips in AC solutions of two concentrations at four pH values. Calcium ion concentrations were measured by ICP-MS.

(1) solubility increases with concentration of AC, (2) solubility increases with decreasing pH and (3) the last trend is linear except at pH 7, where solubility is lower than expected.

The first observation that solubility increases with the concentration of AC must be attributed to the chelating effect that results in the formation of calcium-citrate complexes. Since more citrate is available in the more concentrated solutions, more calcium is chelated. Figure 3 shows that the more concentrated solution dissolves about twice as much calcium as the weaker solution.

The second trend is consistent with the effect of pH generally observed for water on marble and other calcareous minerals [19, 25–27]: a lower pH increases the dissolution of calcite. The action of water on calcite is summarized by the equations:

$$CaCO_3 + H_2O \rightleftharpoons Ca^{2+} + HCO_3^- + OH^-$$
$$CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$$
$$CaCO_3 + H_2CO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

The dissolution of carbonate minerals necessarily involves the carbonic acid system, and the most important parameter controlling carbonate ion activity is pH [23]. The pH of the AC solution was found to have about the same impact as its concentration. The concentration of Ca^{2+} ions in equilibrium with a solution of AC 5% at pH 10, for instance, is similar to that of AC 2% at pH 7.

The third observation that dissolution at pH 7 is lower than expected reflects opposite influences of chelation and pH. The distribution of the different citrate ions ($H_2Citrate^-$, $HCitrate^{2-}$, $Citrate^{3-}$) calculated from dissociation constants varies with pH (see Figure 1) and has a direct influence on the chelating capability for Ca^{2+}. At pH 8 and higher, citrate is deprotonated ($Citrate^{3-}$) and chelates more effectively than at lower pH, where hydrogen ions occupy the coordinating carboxyl groups and prevent calcium ions from binding to the citrate ions [19]. At these higher levels of pH the solubility of Ca^{2+} varies linearly with pH, since the solution contains nearly 100% $Citrate^{3-}$ ions. At pH 7, in contrast, the solution contains 20% $HCitrate^{2-}$ ions, which makes it less efficient in chelating the calcium ions. Therefore, while a lower pH tends to increase the solubility of Ca^{2+}, the lower chelating capacity of citrate at pH 7 attenuates this effect, resulting in solubility almost equal to that found at pH 8.

Impact on gloss after cleaning with a range of AC solutions

For the first series of cleaning tests on marble tiles measured with the glossmeter, variations in gloss (ΔG_{norm}) after cleaning with AC solutions follow the same trends as solubility of Ca^{2+}. Damage to surfaces increases with higher concentrations of AC and decreasing pH (Figure 4). While AC concentration was found to be as important as pH in determining solubility of marble chips, its impact on gloss proved to be smaller.

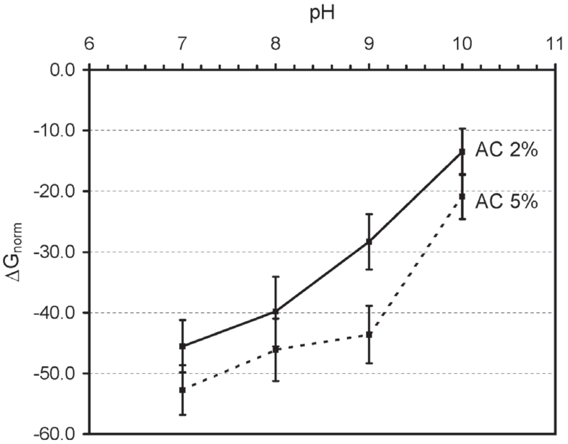

Figure 4 Normalized difference in gloss observed after cleaning marble tiles for four minutes with two concentrations of AC. Lower ΔG_{norm} indicates a higher loss in gloss; thus, a larger damage to the surface.

Whereas about 50% as much Ca^{2+} dissolved for the 2% AC solution as for the 5% solution in the case of the marble chips, the difference in gloss at pH 7 between AC 2% and 5% solutions is about 10 gloss units or only 20% change on the marble tiles. At this level of gloss (c. 60 gloss units), the difference is barely perceptible to the naked eye [28]. There also appears to be a little more difference in gloss between results at pH 7 and pH 8 than for the marble chips, indicating that the lower chelating ability of AC at pH 7 had less impact on the marble tiles, probably because there was sufficient citrate available.

Differences in dissolution between marble chips and marble tiles can be explained by the fact that applying a cleaning solution for a short time is governed by dissolution kinetics rather than the final (thermodynamic) solubility of calcium ions. The dissolution mechanism involves a series of different chemical and physical processes. These steps generally include at a minimum [27]: (1) transport of reactants (citrate ions, H^+ ions) to the solid–liquid interface, (2) adsorption of the reactants onto the surface, (3) reaction(s) between the adsorbed reactant and the solid (this step can involve many intermediate and parallel reactions, e.g., dissociation between Ca^{2+} and CO_3^{2-}, complexing between citrate and Ca^{2+} ions, H^+ attack, hydration or dehydration of the reactants and products, etc.), (4) desorption of the products and (5) transport of the products (in this case calcium citrate) away from the solid–liquid interface. The slowest step determines the dissolution rate, as the reaction cannot proceed faster than the rate-limiting step. When step 1 or 5 is slowest, dissolution is said to be diffusion-controlled. Steps 2, 3 and 4 occur at the surface, and dissolution is said to be surface-controlled when one of these steps is rate controlling. Within the pH range investigated (neutral to alkaline solutions), the dissolution of calcite has been shown to follow a mixed regime, depending on both the mass transfer properties of the solution (steps 1 and 5) and the kinetics of the heterogeneous reactions at the carbonate surface (steps 2 to 4) [19]. In this study, the marble tile is covered with a solution that is unstirred, resulting in a very low mass transfer rate (low steps 1 and 5) [29]. Therefore, the calcium citrate formed during dissolution of the marble accumulates near the surface, preventing fresh free citrate ions from approaching the surface and further complexing calcium ions. This in turns leads to a decrease in the rate of dissolution. In other words, the small difference observed for ΔG_{norm} between AC 2% and 5% solutions indicates that the concentration in chelating agent, even though playing a role, is not the determining factor governing the dissolution reaction; rather, it is driven by the low mass transfer of the products and is diffusion-controlled.

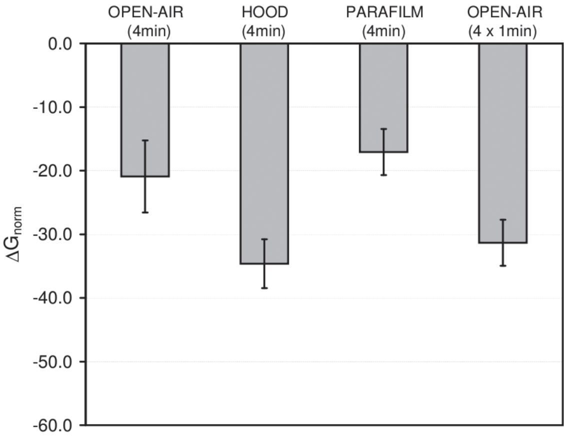

Figure 5 Normalized difference in gloss observed after cleaning marble tiles for four minutes using four modus operandi with a solution of AC 5% at pH 10. Lower ΔG_{norm} indicates a higher loss of gloss and greater damage to the surface.

Influence of the mode of application

Figure 5 shows decreases in gloss measured for areas cleaned using a 5% solution of AC on marble tiles with four different exposures to air, as described for the second series of experiments using the glossmeter. It makes clear that the modus operandi used to clean surfaces affects the amount of damage. Loss of gloss increased by almost 50% when an area was cleaned in a hood with maximum air extraction compared to open-air cleaning for four minutes. This effect is comparable to reducing the pH from 10 to 9 (see Figure 4), and in a way it can be explained by the same process. In a fume hood, the solution covering the marble surface is exposed to a continuous air flow, preventing the liquid–gas interface from achieving a relative equilibrium. The equilibrium between ammonium cations present in the solution and ammonia gas near the solution's surface no longer exists. The evaporation of ammonia is rapid, the equation below is shifted toward the right and pH decreases.

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

Conversely, damage to the surface was slightly reduced by covering the cleaning solution, insuring slower evaporation of ammonia and, thus, a stable pH value. Partial pressure of CO_2 (PCO_2) in the carbonic acid system may also play a role, since exclusion of air results in less dissolution of calcium [23]. At low to neutral pH, atmospheric carbon dioxide is required for charge balance:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^-$$

This effect appears not be very significant here, however, because most of the dissolved Ca^{2+} would be balanced by citrate ions.

Time of application was also found to play a role. Four successive cleanings of one minute were found to be more damaging than a single cleaning of four minutes (Figure 6). When cleaned four times, the change in gloss follows a quadratic trend that can be explained by dissolution kinetics. In the experiment with marble chips it was found that the dissolution of calcium carbonate in citrate solutions was not linear, beginning with a sharp increase in the concentration of calcium and followed by slow convergence toward the solubility value as the solution became progressively less demanding of calcium ions, i.e., the driving force for dissolution was decreasing. Repetition of cleaning with a fresh solution amounts to starting dissolution kinetics anew. As a result, for the same total cleaning time, successive short cleanings are more aggressive than one continuous cleaning. Figure 6 also shows gradual increase in loss of gloss over time, suggesting that poultice cleaning, with its longer exposure time, could be more damaging than the normally short application times when swabs are used.

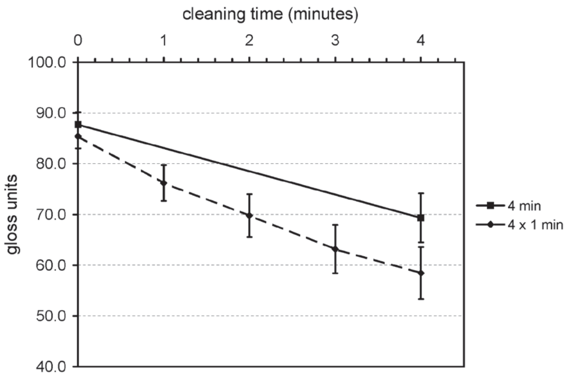

Figure 6 Change of gloss for two series of four-minute cleanings with AC 5% at pH 10 on a marble tile: one consisting of four straight minutes and the other of four cleanings of one minute each.

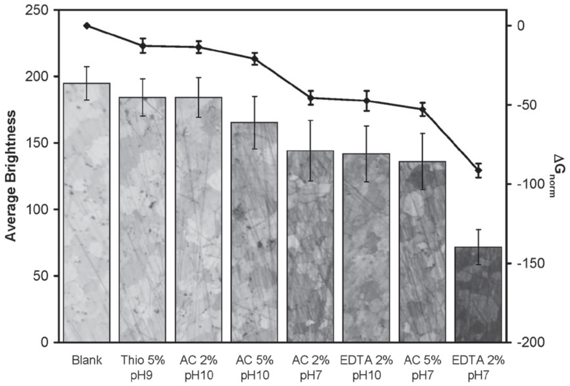

Figure 7 Comparison of AC and other cleaning solutions commonly used for stone, applied to marble tiles. Bars indicate the average brightness measured after cleaning on a scale from 0 (dark) to 250 (light) on the left axis. A typical photograph of each area after cleaning fills its bar. The bold line above the bars indicates normalized differences in gloss on the right axis.

Comparison with other cleaning solutions by gloss and bright-field microscopy

Figure 7 compares gloss and brightness results for AC and two other types of cleaning solutions applied to marble tiles. Once again, the impact of AC depends mainly on pH and concentration. The pH also plays a dominant role in damage by EDTA. At pH 7 AC solutions at both concentrations and the EDTA solution produced 50 or more units of gloss loss and brightness decreases of 25% to 100%. At these levels, damage to surfaces is clearly visible to the naked eye.

Of the comparative cleaning solutions, EDTA 2% (w/v) significantly damaged the marble even at pH 10. This underlines the danger of using EDTA for marble cleaning, in agreement with the literature [20, 24]. By contrast, results for ammonium thioglycolate indicate that it does not damage marble surfaces even at a concentration of 5% and moderate pH. This also agrees with a recent study that suggests its safe use as a cleaning agent for removing rust on marble [30]. However, care should be taken with its use on iron-containing stone. Another study has shown that a 5% (w/v) thioglycolate solution applied to remove iron stains from Globigerina limestone mobilized ferrous ions intrinsic to the stone and brought them to the surface, leading to a heavier staining after treatment [31]. Note that ammonium citrate can be as mild as ammonium thioglycolate at high pH (10) and low concentration, but nearly as aggressive as the EDTA solution at low pH (7) and high concentration.

Figure 7 also shows that gloss measurements and bright-field reflected microscopy gave surprisingly similar results. The average brightness values plotted against ΔG_{norm} produced a straight line with a correlation coefficient R^2 of 0.98, indicating that damage to a polished marble surface may be approximated with this simple microscopic method [18]. More subtle differences, however, require gloss measurements. For example, no difference in brightness was found between cleanings with AC 5% at pH 7 and pH 8 using bright-field reflected microscopy (not shown), while about 10 gloss units difference was measured by the glossmeter.

Implications for conservation treatment

Results of the testing of AC solutions on unweathered, polished marble samples indicate that conservators should keep in mind that AC will damage calcitic stone surfaces by dissolution of the calcite matrix. This dissolution may be invisible to the naked eye [28], but should be taken into account if, for instance, repeated cleaning of the marble is expected. This study also suggests that damage to the stone can be minimized by a careful, optimized design that takes into account the AC solution's pH, concentration and exposure to air during application.

AC solutions at pH 10 produced the least impact on marble test surfaces. In practice, maintaining pH 10 by the addition of ammonium hydroxide is difficult, however, since citrate ions are out of buffer range at pH 10 and even slight evaporation of the ammonia can change the pH significantly. A more practical and pragmatic solution is to use a solution at pH 9, as is often done in practice. Use of a poultice would also serve to provide stability in pH by reducing the evaporation of ammonia. In any case, keeping AC solutions in closed containers and checking the pH of solutions during treatment are good practices.

A lower AC concentration produced less damage on marble test surfaces. To be specific, the 2% AC solution produced less damage than the 5% AC solution. Thus, if a lower concentration is effective, it should be used. However, multiple applications of an AC solution were shown to produce more damage than a single application of the same duration. Thus, if a stronger AC solution is more effective applied once than a weaker solution applied several times, use of the stronger solution may be advisable. As always, testing cleaning solutions on small areas is a good practice to optimize results before treatment commences. The reflected bright-field microscopy procedure described in this paper may also prove useful for preliminary testing.

Less exposure of marble test surfaces to air during cleaning produced less damage. Hence, cleaning in a space with strong air flow or wind should be avoided, taking into consideration basic safety measures for ammonia, such as insuring necessary ventilation, avoiding inhalation, etc. Covering the solution during application with Parafilm showed a slight decrease in gloss loss, suggesting that application of AC in a poultice might have a similar effect. A poultice would not only decrease the dissolution of calcium ions by reducing evaporation of ammonia, but possibly by lowering the concentration of CO_2. Its use would have to be balanced, however, by the potential detrimental effects of longer exposure.

The tests were conducted on unweathered, polished marble, and the impact of AC solutions on stone coated with organic soiling, iron staining, or gypsum crusts may be quite different. For instance, an AC solution will probably cause less etching on iron-stained marble than it did on the samples used in this study, because citrate chelates Fe(III) more strongly than Ca(II). However, one could almost always expect to have an excess of citrate ions compared to Fe(III) ions in marble, so that some etching of the marble matrix is likely to occur.

The efficiency of removing soiling with ammonium citrate solutions at different concentrations and pH values remains unclear, and it is difficult to test. Some preliminary cleaning tests were conducted using AC solutions at a range of pH values on a dirty weathered marble block from the exterior of the US Capitol in Washington, DC, as well as on polished marble tiles that were artificially soiled using a recipe derived from one used on paintings [13]. While the results (not shown) cannot be considered definitive, they seemed to show slight increases in efficiency with decreasing pH. If these results hold, they suggest that the effectiveness of ammonium citrate for removing difficult soiling is not driven primarily by its properties as a deflocculant, surfactant or wetting agent, whose activities are unaffected by pH. Rather its effectiveness results from its capacity to chelate calcium ions, which is related to pH, as is the capacity of water to dissolve calcium ions at lower pH.

CONCLUSION

Ammonium citrate solutions, popular for cleaning calcareous stone, were tested to determine possible damage on marble using two concentrations, four values of pH and several modes of application. Submersion of marble chips in the solutions and application of the solutions to polished marble tiles showed increased dissolution of calcite and loss of gloss and brightness as pH dropped from values of 10 to 7 and as the concentration increased from 2% to 5%. The least damage to marble tiles was produced when solutions were covered during application, and single cleanings were found to be less damaging than multiple applications for the same length of time. EDTA solutions were found to be more aggressive than ammonium citrate solutions on polished marble, while ammonium thioglycolate solutions had minimal impact, similar to that of the least damaging AC solution (AC 2% at pH 10). Changes were successfully measured using ICP-MS, a glossmeter and reflected bright-field microscopy.

Ammonium citrate represents a good compromise in the conservation field. Indeed, conservators report its successful use in cleaning a wide variety of soiling, staining and stone, and it is found to be one of the least harmful chemical products, not only to the stone matrix but also to conservators and the environment. Nonetheless, there remains a need to develop new cleaning products [15, 31] and to systematically study their impacts on the stone matrix. As was done in this study, it is a good practice to know the distribution of ionic species according to pH before choosing the pH and concentration of a cleaning solution, which can be computed by knowing pK_a values and using software such as Curtipot [22]. There is also a general need for continued investigation of the composition of soiling and its interaction with substrates [32]. Indeed, only a better understanding of the substrate–environment interaction will ultimately help to focus efforts in the right direction and choose wisely between the range of chemical, physical and biological cleaning methods available now and in the future.

ACKNOWLEDGEMENTS

The authors wish to thank Barbara Wolanin, curator at the Architect of the Capitol, for graciously letting them carry out some cleaning trials on a piece of marble from the US Capitol; A. Elena Charola and Jennifer Giaccai, for reviewing the manuscript and giving helpful suggestions; and Richard A. Livingston, for discussion of calcium carbonate solubility.

APPENDIX: METHODS

Preparation of $CaCO_3$-saturated water

Marble powder was poured into a 2 L bottle containing DI water, while the solution was stirred until no more powder could be dissolved. Marble chips were then added, and the solution was stirred regularly to ensure saturation and a stable pH (approx. 9.3).

ICP-MS measurements

In inductively coupled plasma–mass spectrometry (ICP-MS), a digested sample is transported from the sample tube using a peristaltic pump through Tygon tubing and introduced into the ICP-MS torch, where an argon gas plasma capable of sustaining temperatures between 8000 and 10000 K is used to ionize the injected sample. The resulting ions then pass through a two-stage interface (sample and skimmer cones) designed to enable the transition of the ions from atmospheric pressure to the vacuum chamber of the ICP-MS system. Once inside the mass spectrometer (in this case a quadrupole MS) ions are filtered according to their mass/charge ratio, then passed on to the detector, which records only a small atomic mass range at one time. By varying the dwell times for the calcium isotope, the entire analysis took less than 10 seconds for each sample.

After the instrument (Perkin Elmer Elan 6000) was optimized, data were generated for a blank and various concentrations of a calcium solution standard (250, 500, 1000, 1500, 3000, 4500 and 6000 ppb). Following measurement of the blank and standards, the unknown solutions were analyzed. In order to detect instrumental drift that may have occurred during analysis, selected standards and blanks were analyzed throughout the day and all standards were re-analyzed at the conclusion of the investigation. Unknown samples were diluted 200 times with 18 megaohm deionized water, while those samples with higher calcium concentration (as determined from initial testing) were diluted 400 times to prevent saturation of the detector. To allow sufficient time for sample uptake and permit the argon gas plasma to stabilize after the introduction of the solution, data acquisition was started after a 15 second delay.

Gloss measurements

Gloss measurements are based on the ASTM standard of a highly polished, perfectly flat black glass with a refractive index of 1.567 for the sodium D line, which is assigned a gloss value of 100. A BYK-Gardner micro-TRI-glossmeter was used to perform measurements. Because of the high gloss of the polished marble tiles, a 20° geometry was chosen for all analyses; the measurement area was 10 × 10 mm. The instrument was regularly calibrated with the black glass standard.

Prior to any measurement, the surface was gently cleaned with a cotton swab and ethanol, and allowed to dry for one hour. This pre-analysis procedure was found to be necessary for accurate and reproducible gloss values. Surfaces cleaned with AC solutions were allowed to dry for at least 24 hours before measurement.

For analysis on each 10 × 10 cm marble square, multiple specular gloss readings were recorded and averaged. The necessary number of readings to get a representative average gloss value was estimated to be 100 readings, randomly distributed on the surface. Typically, two series of 100 readings were performed, giving two gloss averages and standard deviations, respectively $G\underline{1} \pm s\underline{1}$ and $G\underline{2} \pm s\underline{2}$. The final gloss value G and standard deviation *s* were calculated by the following formulae:

$$G = \frac{G\underline{1} + G\underline{2}}{2} \text{ and } s = \sqrt{\frac{(s\underline{1}^2 + s\underline{2}^2)}{2}}, \text{ respectively.}$$

Difference in gloss measurements were computed by performing the above procedure *before* (reference gloss value: $G_0 \pm s_0$) and *after* cleaning (gloss value: $G \pm s$) of the testing surface. On account of the inherent heterogeneity of the material, reference gloss values G_0 obtained on intact polished marble tiles varied slightly according to the tile and the marble square investigated. In order to remove this variation, the *normalized gloss difference* was calculated and used for analysis purposes:

$$\Delta G_{norm} = \left(\frac{G \times 100}{G_0}\right) - 100 \text{ and } s_{norm} = \sqrt{\frac{(s_0^2 + s^2)}{2}}$$

Microscopy

The technique of using bright-field reflected light to examine surfaces is well established, the most familiar example being microscopy of metallurgical cross-sections. A Leica Z16APO photomicroscope equipped with a bright-field coaxial illuminator was used to produce a similar reflected bright-field effect. The polarizer was set at 180° to accentuate the well-defined grain structure of the marble. The visual magnification selected was 20×, each pixel therefore corresponding to 2.8 μm. The field size for each image was 7.21 × 5.40 mm. Using this technique, the most reflective areas appeared brightest, pores and scratches dark and fine abrasions with lowered overall reflectivity.

Histogram data for each field was used to determine the range from dark (roughest) to light (smoothest), and an appropriate exposure length was set for all measurements. In this way, one exposure setting allowed test areas to be compared. The brightest (smoothest) field was the blank or control; the darkest (roughest) was the area to which EDTA 2% at pH 7 had been applied. The rectangular field within the circular droplet was confirmed to be representative by measuring pixel values for 20% of the field, which compared favorably.

Since color information was not helpful for comparison of test areas, a copy of each image was converted to grayscale. Histogram data were computed, and average brightness for each field was calculated based on these data. Changes resulting from increased surface roughness compared to the control surface were fairly easy to see with the naked eye in most test areas.

MATERIALS AND SUPPLIERS

Ammonium citrate, tribasic anhydrous (97% purity), CAS-number 3458-72-8: Sigma-Aldrich, 3050 Spruce St, St Louis, MO 63103, USA.

Ammonium hydroxide (10–35% NH_3), CAS-number 1336-21-6: Fisher Scientific Company, 2000 Park Lane Drive, Pittsburgh, PA 15275, USA.

Thioglycolic acid (≥ 98% purity), CAS-number 68-11-1: Sigma-Aldrich.

EDTA calcium disodium salt, CAS Number 62-33-9: Sigma-Aldrich.

Marble chips (calcium carbonate), CAS-number 471-34-1: Fisher Scientific.

Polished white marble tiles: Morris Tile, 2525 Kenilworth Avenue, Tuxedo, MD 20781, USA.

Parafilm M laboratory wrapping film, Catalog number 13-374-10, Pechiney Plastic Packaging: Fisher Scientific.

REFERENCES

1 Normandin, K.C., and Slaton, D., 'Cleaning techniques', in *Stone Conservation: Principles and Practice*, ed. A. Henry, Donhead, Shaftesbury (2006) 127–160.

2 Vergès-Belmin, V., 'Towards a definition of common evaluation criteria for the cleaning of porous building materials: A review', *Science and Technology for Cultural Heritage* **5** (1996) 69–83.

3 Tabasso, M.L., and Simon, S., 'Testing methods and criteria for the selection/evaluation of products for the conservation of porous building materials', *Reviews in Conservation* **7** (2006) 67–82.

4 Smulders, E., *Laundry Detergents*, Wiley-VCH, Weinheim (2002) 195.

5 Stambolov, T., and Moll, E., 'Derusting of iron drills found on sunken Dutch ships', in *ICOM Committee for Conservation 3rd Triennial Meeting, Madrid, 2–8 October 1972* (1972).

6 Wolbers, R., *Cleaning Painted Surface: Aqueous Methods*, Archetype, London (2000).

7 Pearlstein, E., 'Conservation of three New Kingdom statues in the Colonnade Hall of the Luxor temple, Egypt', in *The Materials, Technology, and Art of Conservation: Studies in Honor of Lawrence J. Majewski*, ed. A. Rushfield and M. W. Ballard, Conservation Center of the Institute of Fine Arts, New York University, New York (1999) 217–256.

8 De Bazelaire, H., Gervais, C., and Piffaut, C. *Restauration de douze Médaillons en marbre du XVIIème siècle, Eglise de Versailles*, internal report, Conservateur régional des monuments historiques, Île de France (2005).

9 Matero, F.G., and Tagle, A.A., 'Cleaning, iron stain removal, and surface repair of architectural marble and crystalline limestone: The Metropolitan Club', *Journal of the American Institute of Conservation* **34** (1995) 49–68.

10 Gale, F.R., and Weiss, N.R., 'A study of examination and treatment techniques for a limestone gazebo', in *Proceedings of the Fourth International Congress on the Deterioration and Preservation of Stone Objects, Louisville, 7–9 July 1982*, ed. K.L. Gauri and J. A. Gwinn, University of Louisville, Louisville, KY (1982) 135–145.

11 Carlyle, L., Townsend, J.H., and Hackney, S., 'Triammonium citrate: An investigation into its application for surface cleaning', in *Dirt and Pictures Separated*, ed. S. Hackney, J. Townsend and N. Eastaugh, UKIC, London (1990) 44–48.

12 Hilfrich, U., and Weser, U., 'The cleaning of varnish coated paint surfaces by ammonium citrate', *Zeitschrift für Kunsttechnologie und Konservierung* **17** (2003) 85–94.

13 Phenix, A., and Burnstock, A., 'The removal of surface dirt on paintings with chelating agents', *The Conservator* **16** (1992) 28–38.

14 Mansmann, K., 'Oberflächenreinigung mit Ammoniumcitraten', *Zeitschrift für Kunsttechnologie Kunsttechnologie Konservierung* **12** (1998) 220–237.

15 Cushman, M., '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', in *ANAGPC 2006 Student Papers Presented at the 2006 Annual Student Conference, University of Delaware/ Winterthur Art Conservation Department*, www.ischool.utexas.edu/~anagpic/studentpapers2006.htm (accessed 29 April 2010).

16 Pierre, J.L., and Gautier-Luneau, I., 'Iron and citric acid: A fuzzy chemistry of ubiquitous biological relevance', *BioMetals* **13** (2000) 91–96.

17 Lazzarini, L., Professor of Applied Petrography in the Faculty of Architecture of the University IUAV of Venice, personal communication (June 2008).

18 Grissom, C.A., Charola, A.E., and Wachowiak, M.J., 'Measuring surface roughness on stone: Back to basics', *Studies in Conservation* **45** (2000) 73–84.

19 Fredd, C.N., and Folger, H.S., 'The influence of chelating agents on the kinetics of calcite dissolution', *Journal of Colloid and Interface Science* **204** (1998) 187–197.

20 Thorn, A., 'The impact of disodium EDTA on stone', in *ICOM Committee for Conservation 10th Triennial Meeting, Washington, DC, 22–27 August, 1993*, ed. J. Bridgland, ICOM, Paris (1993) 357–363.

21 Ricciardi, L., 'I mosaici paleocristiani di cimitile presso nola (Na), tra abbandono e restauro', *Progetto Restauro* **45** (winter 2008) 37–44.

22 'Curtipot: A freeware for pH and acid-base equilibrium calculations and for simulation and analysis of potentiometric titration curves', http://www2.iq.usp.br/docente/gutz/Curtipot.html (accessed 29 April 2010).

23 Livingston, R., 'Geochemical considerations in the cleaning of carbonate stone', in *Stone Cleaning and the Nature, Soiling and Decay Mechanisms of Stone*, *Proceedings of the International Conference, Edinburgh, 14–16 April 1992,* ed. R.G.M. Webster., Donhead, London (1992), 166–179.

24 Lauffenburger, J.A., Grissom, C.A., and Charola, A.E., 'Changes in gloss of marble surfaces as a result of methylcellulose poulticing', *Studies in Conservation* **37** (1992) 155–164.

25 Orkoula, M.G., and Koutsoukos, P.G., 'Dissolution of Pentelic marble at alkaline pH', *Langmuir* **16** (2000) 7263–7267.

26 Kanellopoulou, D.G., and Koutsoukos, P.G., 'The calcitic marble/water interface: Kinetics of dissolution and inhibition with potential implications in stone conservation', *Langmuir* **19** (2003) 5691–5699.

27 Morse, J.W., and Arvidson, R.S., 'The dissolution kinetics of major sedimentary carbonate minerals', *Earth-Science Reviews* **58** (2002) 51–84.

28 Obein, G., Knoblauch, K., and Viénot, F., 'Difference scaling of gloss: Nonlinearity, binocularity, and constancy', *Journal of Vision* **4** (2004) 711–720.

29 Al-Khaldi, M.H., Nasr-El-Din, H.A., Mehta, S., and Al-Aamri, A.D., 'Reaction of citric acid with calcite', *Chemical Engineering Science* **62** (2007) 5880–5896.

30 Thorn, A., 'Treatment of heavily iron-stained limestone and marble sculpture', in *ICOM Committee for Conservation 14th Triennial Meeting: The Hague, Netherlands*, *12–16 September 2005,* ed. I. Verger, James & James, London (2005) 888–894.

31 Vella, D., Hadj Amar, A.B., and Chetcuti, F., 'A preliminary investigation of the removal of rust stains from Globigerina limestone surfaces using coupled chelating-reducing systems', in *Proceedings of the 11th International Congress on Deterioration and Conservation of Stone, Torun, Poland*, *15–20 September 2008,* ed. J. Ciabach, Nicholas Copernicus University, Torun (2008) 1093–1100.

32 Bonazza, A., Sabbioni, C., and Ghedini, N., 'Quantitative data on carbon fractions in interpretation of black crusts and soiling on European built heritage', *Atmospheric Environment* **39** (2005) 2607–2618.

AUTHORS

CLAIRE GERVAIS is a visiting scholar at the Smithsonian Institution's Museum Conservation Institute, USA. She received her MS degree in material sciences and PhD degree in physical chemistry at the University of Rouen, France. Following two postdoctoral fellowships on the prediction of physical properties of organic molecular crystals and proteins, she is now focusing her interests towards conservation science, with an emphasis on stone conservation, structural and chemical investigation of pigments and use of synchrotron techniques for the study of cultural heritage. *Address: Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Road, Suitland, MD 20746, USA. Email: gervaisc@si.edu, gervais.claire@gmail.com*

CAROL A. GRISSOM has been a senior objects conservator at the Smithsonian Institution since 1984, specializing in treatment of metal, plaster, and stone sculpture. She received a MA degree in art conservation from Oberlin College, Ohio, USA, undertook advanced training in Belgium and Italy, and has worked as a sculpture conservator at the Center for Archaeometry, Washington University, St Louis, and exhibitions conservator at the National Gallery of Art, all in the USA. *Address: as Gervais. Email: grissomc@si.edu*

NICOLE LITTLE is a physical scientist at the Smithsonian Institution's Museum Conservation Institute. She received both her BA and MA in anthropology from the University of Missouri-Columbia, USA where her master's research dealt with the compositional analysis of Mayan ceramics from northwest Belize. Her areas of interest include the application of inductively coupled plasma–mass spectrometry and X-ray diffraction to the technical study of museum objects. *Address: as Gervais. Email: littlen@si.edu*

MELVIN J. WACHOWIAK is a senior conservator at the Smithsonian Institution's Museum Conservation Institute. He has a background in studio art, as well as a graduate degree in Conservation. He has been at the Smithsonian since 1989, and involved in projects in the fine arts, anthropology and archeology and the history of technology collections. Areas of expertise include digital imaging, microscopy and 3D scanning, as well as preservation of collections. *Address: as Gervais. Email: wachowiakm@si.edu*

Résumé — *On a testé des solutions de citrate d'ammonium afin de déterminer les dommages possibles sur le marbre, en utilisant deux concentrations différentes, quatre valeurs de pH, et plusieurs variantes dans les modalités d'application. Pour un pH mesuré de 10 à 7, les microplaquettes de marbre immergées dans les solutions ont montré une dissolution décroissante de la calcite, et les carreaux de marbre sur lesquels les solutions ont été appliquées ont montré une perte croissante de clarté et de brillance. Les dommages les moins importants sur les carreaux de marbre se sont produits quand les solutions étaient recouvertes pendant l'application, et, pour un même temps d'application, un nettoyage simple s'est révélé moins dommageable que des nettoyages multiples. La comparaison avec d'autres agents de nettoyage – thioglycolate d'ammonium et EDTA – ont montré que la solution de citrate d'ammonium pourrait s'avérer plus douce sous certaines conditions, telles qu'un pH élevé et une faible concentration. En revanche, le citrate d'ammonium pourrait agresser la pierre de façon significative s'il est utilisé dans l'autres conditions, comme un pH de 7 ou une ventilation forte. Dans ces cas-là, les dommages étaient presque identiques à ceux d'une solution à 2% d'EDTA avec un pH de 10. Cette étude souligne la nécessité de développer de nouveaux produits de nettoyage, recherche qui ne peut se faire qu'en rapport étroit avec une meilleure compréhension des diverses interactions entre l'agent de nettoyage, le substrat et l'environnement.*

Zusammenfassung — *Lösungen von Ammoniumcitrat wurden in zwei Konzentrationen, vier verschiedenen pH-Werten und zahlreichen verschiedenen Applikationsmethoden getestet, um eine mögliche Schadensbildung auf Marmor zu bestimmen. Als der pH-Wert sich von 10 nach 7 veränderte, löste sich Calcit verstärkt und mit der Lösung behandelte polierte Marmorkacheln verloren zunehmend an Glanz und Helligkeit. Die geringsten Schäden an den Marmorkacheln entstanden, wenn die Lösungen während der Applikation abgedeckt waren. Darüber hinaus waren einzelne Anwendungen weniger schädigend als mehrmalige. Im Vergleich mit anderen Reinigungsmitteln - Ammoniumthioglycolat und Ethylendiamintetraessigsäure* (*EDTA) – zeigte sich, daß Ammoniumcitrat so mild wie Ammoniumthioglycolat sein kann, aber nur dann, wenn es unter den gleichen Bedingungen, also mit hohem pH-Wert und geringer Konzentration, angewendet wird. Im Gegensatz dazu zeigten Ammoniumcitratlösungen bei pH-Wert 7 und starkem Lufteintrag große Schäden an den Steinen. In diesen Fällen entsprach der Schaden einer 2%igen EDTA – Lösung bei pH 10. Die Studie unterstrich die Notwendigkeit der Entwicklung neuer Reinigungsmittel, eine Forschung, die nur Hand in Hand mit einem besseren Verständnis der zahlreichen Wechselwirkungen zwischen Reinigungsmittel, Substrat und Umwelt erfolgen kann.*

Resumen — *Para este estudio se probaron disoluciones de citrato amónico, en dos concentraciones diferentes, con diferentes valores de pH y variaciones en su aplicación, con el fin de determinar el posible daño inflingido al mármol. A medida que el valor del pH iba cayendo de 10 a 7, fragmentos de mármol sumergidos en las disoluciones mostraron un aumento de la disolución de la calcita, y baldosas de mármol pulido a las que se aplicó las mencionadas disoluciones, mostraron un aumento en la pérdida de brillo y de lustre. El menor daño a estas baldosas se produjo cuando las disoluciones se daban a cubierto, y las limpiezas sencillas se mostraron menos dañinas que las limpiezas múltiples, con un tiempo de aplicación idéntico. La comparación con otros agentes de limpieza – tioglicolato de amonio y ácido etilendiaminatetraacético (EDTA) – mostraron que las disoluciones de citrato amónico podían ser tan suaves como las de tioglicolato cuando se usan en determinadas circunstancias, como a elevados pH y bajas concentraciones. Por el contrario, las disoluciones de citrato de amonio pueden dañar la piedra de forma significativa cuando son usadas bajo otras condiciones, como un pH 7 o alta ventilación. En estos casos el daño es similar a una disolución de EDTA al 2% y un pH 10. Esta investigación resalta la importancia y necesidad de desarrollar nuevos productos de limpieza; esta búsqueda sólo puede ir de la mano de un mejor conocimiento de las variadas interacciones que tienen lugar entre agente de limpieza, sustrato y ambiente.*