

THE TREATMENT OF IRON-STAINED MARBLE: TOWARD A “GREEN” SOLUTION

Andrea MACCHIA¹, Silvestro A. RUFFOLO^{2*}, Laura RIVAROLI¹, Mauro F. LA RUSSA²

¹ YOCOCU, Youth in Conservation of Cultural Heritage, Largo dei Quintili 21, 00175 Roma, Italy

² Università della Calabria, Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST), Via Pietro Bucci, 87036 Arcavacata di Rende (Cs), Italy

Abstract

In the field of stone restoration, an unresolved issue is represented by the removal of iron stains from stone substrates. This study deals with a comparative study of the efficacy of several formulations in removing iron-stains from marble. These formulations are mostly based on chelating agents (ammonium thioglycolate, ammonium citrate, L-cysteine and DL methionine), which can form stable complexes with iron. Two sets of experiments have been carried out. Powdered calcium carbonate has been mixed with ferric hydroxide, then the mixture has been put in contact with the formulations, then the amount of removed iron has been evaluated. Another experimentation has been carried out on marble specimens artificially stained with rust. Removing tests have been performed, and their efficiency has been evaluated by measuring the colorimetric variations of the surfaces and the variation of the porous structure. The use of cysteine together with sodium dithionite solution showed the best results; moreover this formulation is the most eco-friendly solution, both for the restores and for the environment.

Keywords: Iron stains removal; Stained marble; Chelating agents; Ammonium thioglycolate; Ammonium citrate; L-cysteine; DL methionine

Introduction

When metal and stone are used together in the same artworks, some conservation problems can arise [1]. A stone commonly used in cultural heritage objects is marble; often it shows a brownish staining due to contact with iron or its alloys [2-3]. Therefore, the corrosion products, can be dissolved and washed out by rain, but part of them can penetrate into the stone, thanks to water and to the porous structure of the stone. This lead to the formation of orange to brownish colour rust stains, which alter the appearance of the stone surface, this is undesirable from an aesthetic point of view. The stains consist of a variety of Fe(III) oxyhydroxides or hydrated oxides of high stability and low solubility. Generally, the concentration of these iron oxides decreases from the stone surface toward its core, and their formation and nature depend on their solubility parameters and on the environmental condition [3]. The formed species depend on the pH value and on the presence of different anions. It is generally accepted that the

* Corresponding author: silvestro.ruffolo@unical.it

rust is composed of ferrihydrite and α -, β - and γ -FeOOH (goethite, akaganeite and lepidocrocite) [4-6]. These investigations have shown that goethite defines a thermodynamic minimum of the rust system and the solubility product of goethite ($K_{ps} = 10^{-41}$) is the lowest among the different rust species [5-6]. This means that rust can be considered as goethite, and thus the cleaning of rust can be considered as removal of goethite.

Common cleaning methods are based on different chelating and reducing agents mixed in a poultice and placed onto the stone surface. Chelating agents are organic or inorganic compounds capable of binding metal ions to form complex ring-like structure called 'chelates'. Chelating agents possess "ligand" binding atoms that form either two covalent linkages, or one covalent and one co-ordinate, or two co-ordinate linkages in the case of bidentate chelates [7].

Formulations, containing reducing agents that can weaken the bonds between iron atoms in the iron oxide are the most efficient ones [8]. This is achieved by reduction of surface Fe(III) ions to Fe(II) and it depends on the pH, temperature and redox potential [9]. A wide range of reducing agents has been employed for the dissolution of iron oxides [10]. One of the ligands most widely used is the citrate ion or salts of other carboxylic acids, such as oxalic, ascorbic and tartaric acid [11-15].

Other methods involve the use of EDTA [16]. A relatively new method is the use of the hexadentate ligand TPEN [17], which, in contrast to EDTA, has a high affinity towards iron and a low affinity towards calcium. The ligands are used either alone or in combination with reducing agents such as thiosulfate, dithionite or polythiophene. Thioglycolate salts have been applied in several conservation treatments of calcareous stone [18]. Thioglycolate is presumably the most efficient ligand for cleaning rust stained marble, however, thioglycolic acid is a toxic compound.

This paper is aimed to compare the efficiency of several ligands in removing iron stains from marble substrate. For this purpose, powdered calcium carbonate has been mixed with ferric hydroxide, then the mixture has been put in contact with several chemicals, it has been assessed for each treatment, the amount of solubilized iron from the powder. At the same time, it has been measured the amount of calcium in solution; the latter evaluation is aimed to understand the aggressiveness of the removing agents toward the marble substrate. Another experimentation has been carried out on marble specimens artificially stained with rust. Removing tests have been performed, and their efficiency has been evaluated by measuring the colorimetric variations of the surfaces and the variations of the porous structure. The goal of the paper is to validate those methods, which exclude, or at least limit the use of compounds and solvents harmful for the restorers and for the environment.

Experimental

Materials

The selection of the reagents to test was primarily based on the following criteria: a) capability to form complex or chelate compounds with iron ions; b) compatibility with the stone surface; c) solubility in water; d) products currently adopted in the conservation treatments. Other features, such as the cost and the availability, were considered as secondary criteria.

The summary of chelating agents selected for the experimentation is reported in Table 1.

An issue of Fe(III) compounds is represented by their very low solubility. Very low pH is required to dissolve them, but a low pH is very damaging toward calcareous stone. Maintaining an appropriate pH is fundamental to preserve the marble. Furthermore, most chelating agents are unstable at low pH values, whereas at high pH values, metals tend to form insoluble hydroxides, which are less accessible to chelating agents.

In this research, sulphide-containing chelators similar to thioglycolate were examined. It is well known the chelating ability of methionine and cysteine [19], two sulfhydryl-containing compounds, which are the main sulfur-containing amino acids and that. These amino acids form complexes with Fe(III) and Fe(II) with high stability constants, and only very weak complexes with Ca(II) and Mg(II) [19].

Table 1. Selected chemicals

Chelating agents	pH	Concentration	Note
Ammonium thioglycolate	9	5% (w/v)	
Ammonium citrate	10	2% (w/v)	
L-cysteine + sodium dithionite (SD)	8	0.1M + 0.1M	pH value adjusted with ammonium hydroxide
L-cysteine + DL methionine + SD	8	0.1M + 0.05M+0.1M	
Metal Rescue™ Rust Remover	6.5	-	

Cysteine reacts as a reducing agent in the Fe(III)-complexes, leading to the formation of colourless complexes, while the methionine forms complexes especially with Fe(II). Cysteine is also susceptible to oxidation, forming disulfide bonds with neighboring cysteine residues, generating a violet insoluble complex in water.

For this reason, the adding of sodium dithionite (SD) together with cysteine prevents the precipitation of cysteine [20-21].

With respect to cysteine, the methionine is a non-polar, aliphatic amino acid with antioxidant characteristic. Cysteine and methionine are used in combination for the chelation and excretion of metals from the human body [7].

Metal Rescue™ Rust Removers is a commercial product used for remove rust on several materials. The solvent is organic, the active compounds (whose composition it is not declared by the producer) can provide sulphur to form ferric sulphate in combination with an iron-chelator complex, this allows the chelator to remove more iron from iron oxide. Finally, ammonium thioglycolate and ammonium citrate, have been also tested. These are chelating agents commonly used by conservators to remove iron stains from marble.

Methods

The comparative study of the cleaning methods (highest extraction rate of iron, lowest extraction rate of calcium) was achieved by carrying out two parallel experimentations, specified as follows:

- a) Tests on a powder mixture of calcium carbonate and ferric hydroxide oxide (ALDRICH–325 mesh) using all the above listed reagents. The experiments were carried out in triplicate. Powdered mixture (Fe/Ca = 2/100) was treated with 25mL of each extracting solution (five) into glass flask, and left under stirring at room temperature. At fixed times (15, 30, 60, 90, 180, 300min) each solution was filtered through a 0.2mm Cellulose acetate filter and after a 1/100 dilution by deionized water, the Fe and Ca concentrations were determined by ICP/OES (Varian Inc. e Vista MPX Simultaneous ICP-OES).

- b) Test on artificially stained marble blocks. A total of 45 Carrara marble blocks (5×5×2cm in size) were used for the test. All the blocks were preliminarily brushed, washed and dried in an oven at 60±2°C, with forced ventilation for 7 days, until they reached a constant weight. To stain the blocks, iron sheets were applied on the marble surface and degraded using accelerated 6 h stress cycle in climate chamber: temperature - humidity relative: 30°C/70% - 10°C/100% (Fig. 1). After 1 month of cycles, the colour of surfaces was also measured by a colorimeter MINOLTA CM-2002.

The colour of each set of three blocks was measured again after the iron staining. To evaluate the superficial alteration induced by the cleaning solution, water absorptivity measurements were carried out according to UNI 10859:2000 [22], on original and cleaned blocks. The superficial alteration can induce some changing in quantity, sizes and connection of pores and consequently could influence the absorption rate [23-27]. The stained blocks were cleaned according to the following procedure: a 5×5cm sheet of Japanese paper was put in contact with the block surface and covered with a poultice made with cellulose pulp containing 10% w/w of sepiolite, wet with the cleaning solution or deionized water. Each block was subjected to one and three cycles of cleaning with the cleaning solutions; then they were washed with deionized water; both the reagents and water were applied as poultices of cellulose pulp and sepiolite.



Fig. 1. Stained marble block

Results and Discussion

Tests on powder mixtures

Figure 2 shows the amount of extracted Fe in function of time, while figure 3 shows the values of extracted Ca expressed as percentage.

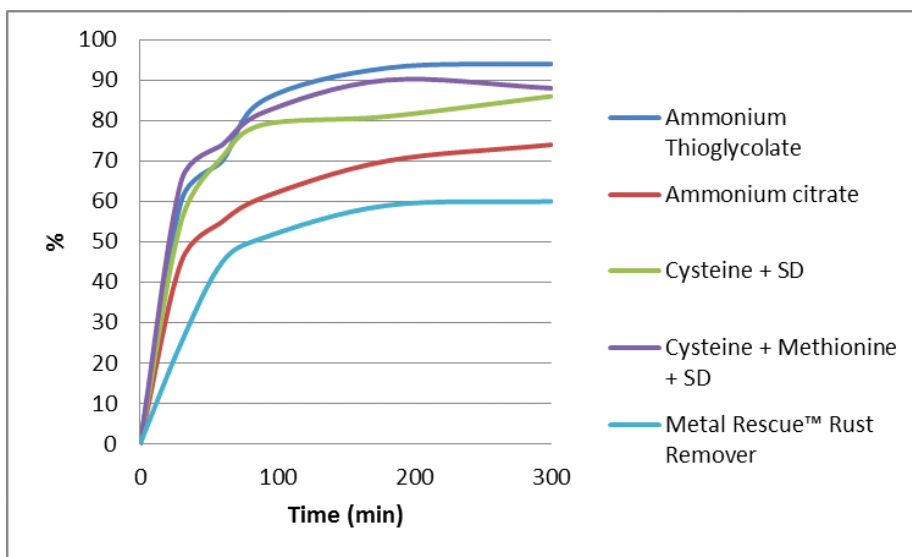


Fig. 2. Amount of iron (% wt) extracted by the cleaning solutions, as a function of the time

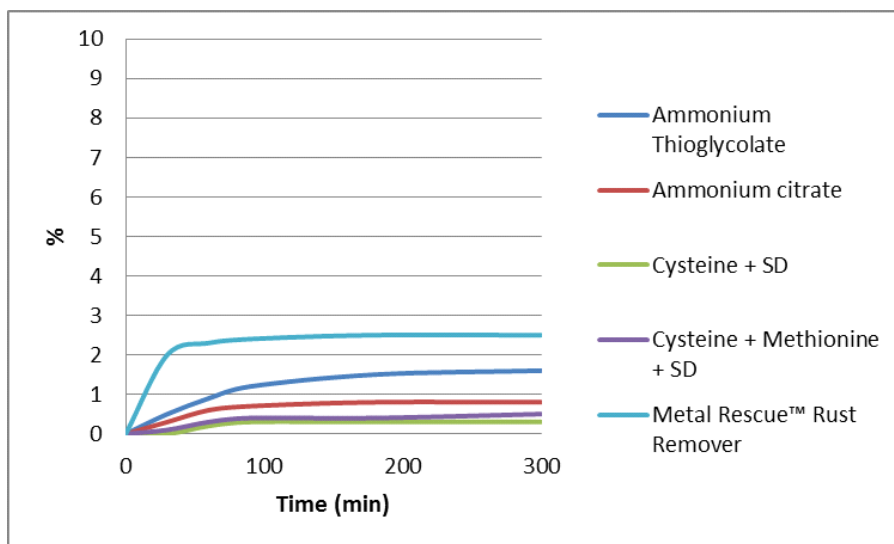


Fig. 3. Amount of calcium (% wt) extracted by the cleaning solutions, as a function of the time

Both graphs are referred to the extracted ion with respect to the original powder mixture of calcium carbonate and ferric hydroxide oxide. As illustrated in figure 2, ammonium thioglycolate demonstrated a very high solvent power on the iron and low impact on the calcium. The thiol group in cysteine has a high affinity for iron and the addition of sodium dithionite preserves the oxidation of cysteine showed good iron solubilization and low amount of extracted calcium. The combined treatment, cysteine and methionine, with SD, was more effective with respect to the only cysteine+SD, due to the high affinity of the methionite with Fe(III) at pH = 8.0 [28].

The efficiency of ammonium citrate and of Metal Rescue to remove iron is similar, but the Metal Rescue removed more calcium with respect to citrate.

Test on artificially stained marble blocks

In order to define the colorimetric parameters before and after the cleaning, the superficial colour of each block was analysed in five different areas. As an example of the cleaning results, in figure 4 it has been reported the set of curves related to the samples cleaned with cysteine+SD. The stained samples had maximum reflectance at about 650 nm (which corresponds to the Red and Yellow CIE chromatic interval), while the cleaned samples regained the chromatic characteristics of the original marble, as shown by the close similarity of the corresponding curves.

For a better evaluation of the cleaning effects produced by the solutions, the chromatic parameters were expressed as differences of $L^*a^*b^*$ coordinates between cleaned and untreated marble blocks, acquired after one cycle and three cycles of cleaning [29, 30].

The results are summarized in figure 5, which reports the average $L^*a^*b^*$ values obtained on three blocks. The cleaning procedures carried out with cysteine + methionine + SD produced surface colour closer to the untreated marble than that those treated with ammonium thioglycolate. The smaller differences were obtained when cysteine + SD and ammonium citrate were used, while Remover did not produce a complete removal of the chromatic alteration of surfaces.

The picture in figure 6 shows the specimens after the stain removal tests. The images are coherent with the results obtained by colorimetric and ICP/OES measurements. In particular, the blocks treated with Remover remained partially stained after the cleaning. The block treated with ammonium thioglycolate showed a rough surface respect to untreated blocks.

The water adsorption by capillarity was carried out on fifteen marble blocks. The aim was to detect, in an indirect way, alteration induced by the cleaning solution on the surface, since the capillary absorption dynamics is sensitive to the surface and to the porous structure.

Figure 7 shows the difference, expressed in terms of capillary absorption coefficient (CA), between cleaned and untreated marble block, in function of time. Only the Remover and ammonium thioglycolate changed slightly the CA in the early stage of the adsorption curve.

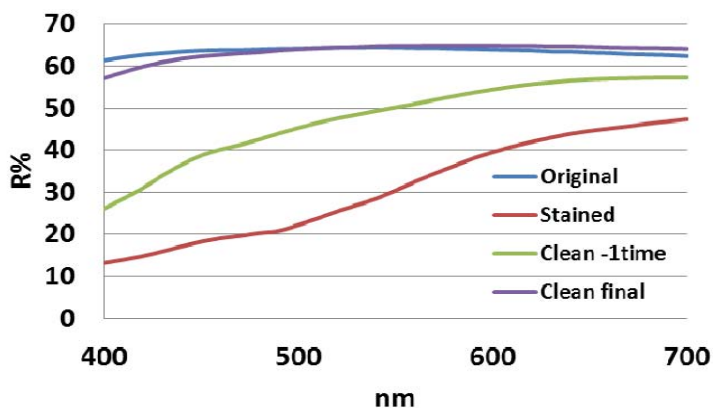


Fig. 4. Visible spectra on stained marble block: Original - original colour of marble; stained: stained blocks; clean -1time - colour surface then the application of one cycle of cleaning; Clean final - colour surface then the application of three cycle of cleaning

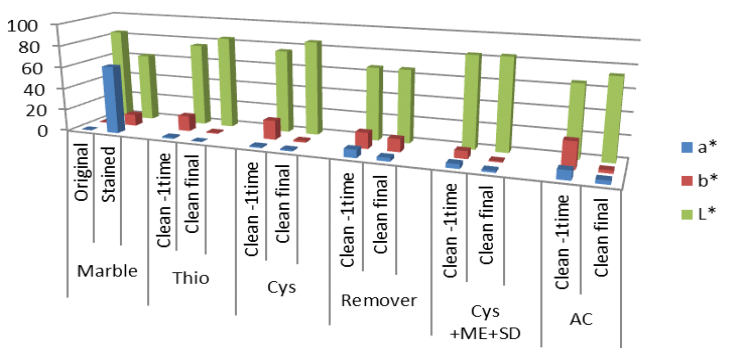


Fig. 5. Comparison of L*a*b* coordinates of untreated and cleaned marble blocks. Marble - untreated specimens; Stained - stained block; Thio - ammonium thioglycolate; Cys - L-Cysteine + sodium dithionite (SD); Remover - Metal Rescue™ Rust Remover; L-cysteine + DL-methionine + SD; AC - ammonium citrate



Fig. 6. Stained and cleaned marble specimens

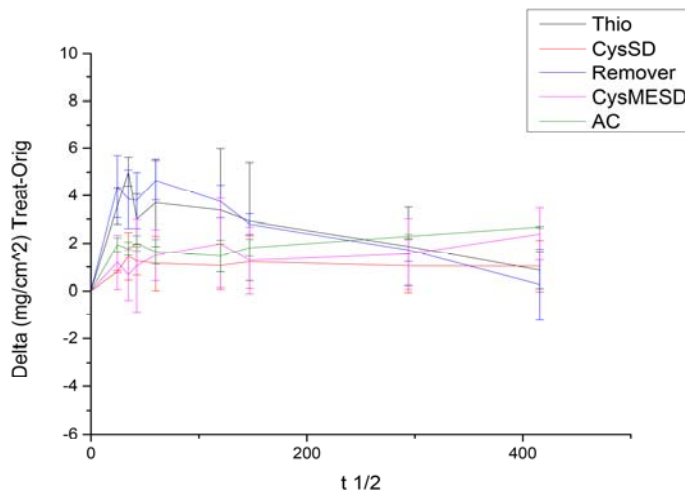


Fig. 7. Differences between cleaned and untreated marble block capillary absorption coefficient (CA)

Conclusions

Several formulations have been tested to remove iron stains from marble substrate. A systematic approach was adopted, testing and comparing different chemicals, always with complexing features, selected on the basis of different chemical characteristics, the goal was to indicate the most selective agent, which can remove the iron compounds from the stone surface, leaving mostly unaltered the substrate. The use of cysteine together with sodium dithionite solution resulted to respond to those requirements. In addition, this formulation is completely non-harmful for the restores and the environment. The addition of methionine in this formulation was able to improve the removal of iron. This result suggests to the technical-scientific community to continue research in this direction by carrying out an extensive in situ experimentation.

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