Irene Matteini
University of Pennsylvania

An assessment and evaluation on the effects of acidic cleaning methods on unglazed terra cotta using accelerated weathering test protocols
ABSTRACT

According to the published literature, there has been very little quantitative evaluation of the short or long term effects of cleaning terra cotta, other than visual assessment where success is pronounced by the degree of soiling removed. Very little work (only 3% within the literature review) has attempted to measure the effects on terra cotta of various cleaning methods.

Nevertheless today, still 80% of terra cotta cleaning relies on chemical products, the majority acid based. (Boyer, 2014)

This research evaluated the effects of acidic cleaners on unglazed terra cotta to verify the potential for damage by accelerated weathering testing. This investigation started from previous studies (Matero et al., 1996) where findings showed that by using hydrofluoric acid-based commercial cleaning system, an increased porosity of unglazed terra cotta resulted. The questions remains whether this physical alteration will lead to accelerated weathering and material damage.

In this research, two commercial chemical cleaners were tested in two applications on new unglazed red and tan terra cotta samples, and then accelerated weathering testing protocols conducted. Several methods of assessment were used to evaluate the samples before and after testing as optical microscope, scanning electron microscope, porosity by using liquid nitrogen, color change and texture mapping imaging. By examining physical changes and their response to accelerated weathering across two typical terra cotta bodies, it is hoped that better cleaning methods will be considered in practice and parameters to measure potential damage as well as cleaning efficacy.
1. INTRODUCTION

Cleaning has been a major concern for architectural terra cotta since its re-introduction in the 19th century. Despite the relevance of the problem for the increasing number of soiled historical buildings worldwide, the published literature suggests that very little quantitative evaluation of the short or long-term effects or performance of cleaned terra cotta has occurred. Today, success has been pronounced almost exclusively by the degree of soiling removed, frequently by chemical means. (Matteini, 2014) According to David Boyer, president and CEO of ProSoCo, chemical products still account for 80% of all terra cotta cleanings in the United States (Boyer, 2014). Unfortunately very little work has been done to measure and evaluate the effects of these cleaners on terra cotta before and after treatment. Matero demonstrated that by using hydrofluoric acid (HF) based commercial cleaner specifically designed for masonry, increased porosity and potentially increased permeability of the terra cotta occurred. (Matero et al., 1996).

Therefore, this investigation assessed and evaluated the effects of acidic cleaners on unglazed terra cotta in order to verify the potential for accelerated weathering. Two commercial chemical cleaners were tested in two applications: ProSoCo Heavy Duty Restoration Cleaner, an aqueous hydrofluoric acid-based cleaner (1 part cleaner: 3 parts water by volume), and ProSoCo Enviro Klean, an aqueous ammonium bi-fluoride cleaner (applied as a concentrate). The selection of these two products was related to their popularity in the restoration market by architects, conservators, and building contractors, as confirmed by a 2014 field survey and literature review completed. (Matteini, 2014)

In the first phase of this research, a literature review was completed, together with a survey of professionals involved in the restoration of terra cotta buildings as architects, conservators, building contractors and product manufacturers. This data was reported and a timeline was produced and presented at the IIC Architectural Ceramics Conference in March 2014. (Matteini, 2014)

In the second phase, new commercial unglazed terra cotta samples were obtained and treated, and then artificially weathered.
Several methods were used to evaluate and assess the samples before and after accelerated testing protocols by looking at the following properties:

- Morphology and change in porosity by Scanning Electron Microscopy
- Change in porosity by using Liquid Nitrogen Porosimetry
- Change in Surface Texture by Texture Mapping Photography
- Visual & Color change by using a Minolta Spectrophotometer

2. LITERATURE REVIEW ON CLEANING TERRA COTTA

During the 19th century, terra cotta rapidly became the protagonist of the skylines of major American cities. Advertised in early publications (Atlantic Terra cotta Company Magazine, 1917), this material was described as very easy to clean, requiring only a scrubbing and washing with soap.

Ultimately with the proliferation of factories and automobiles, and the increase in urban pollution, terra cotta buildings rapidly soiled and blackened. Unavoidably, cleaning became a major issue and challenged claims of terra cotta’s resistance to soiling.

Overtime a vast array of cleaning techniques have been performed on terra cotta buildings in the attempt to remove soiling: from the earliest techniques of steam cleaning, “sand-blasting,” (Congressional Serial Set, 1913) and soap to the introduction of the first commercial restoration specialty cleaning products in the 1960s (Boyer, 2014). Later more targeted techniques including a range of chemical and micro-abrasive methods have been developed including laser ablation. (Larson, 1994)

The first phase of this research was the updating of an earlier literature review on the conservation of architectural terra cotta together with a survey of professional practices in cleaning terra cotta buildings in the United States by polling architects, artists, engineers, conservators, contractors, and product manufacturers. (Matteini, 2014).

After updating the bibliography, the total number of publications (books, conference proceedings, journal articles, and standards) numbered to 567 spanning from 1893-2014. Only 85 or 15% of the published material addressed the subjects of soiling and cleaning. (Fig. 1) (Matteini, 2014)
Within the 85 entries dedicated to cleaning, 27 publications were represented as case studies (32%), followed by 23 publications describing specific cleaning methods (27%) which account for more than half of the sources found (59%). Hybrid publications addressing two or more of the above subjects in some degree of detail (25%) were next in representation followed by a very low percentage of research on soiling (7%), performance standards (6%), and finally evaluation of cleaning before or after treatment (3%). (Fig. 2) (Matteini, 2014)
By looking at different cleaning techniques overtime, chemical, followed by mechanical methods have remained the most popular according to the literature review, and also confirmed by the survey. (Matteini, 2014) (Fig. 3) Beginning in the early 1980’s, we start to see the introduction of more sophisticated micro-abrasive techniques such as Thoman-Hanry Gommage (Slaton et al., 1994), Jos, Rotec Quintex (Varalli, 2014), and Sponge-Jet (Valoria, 2014), together with the rise of laser cleaning with its first application on terracotta in 1994 at the Victoria Albert Hall. (Larson, 1996)

Furthermore, the introduction of tighter environmental safety controls also encouraged the launch of these newer techniques in the market (Rossol, 2014). At the same time, the use of steam, as one of the oldest techniques, shows an oscillation of popularity in response to problems related to the misuse of chemical and mechanical systems. In the last ten years, again chemical cleaning has shown a similar level of interest. (Boyer, 2014)

In conclusions despite the long observed problem of soiling on terracotta buildings, the literature review and the survey suggested that very little is known about the mechanisms of soiling with only few exceptions (Moynehan et al., 1995; Hall, 2003; Hall, 2011). Even less
is known about the effects on the substrate of the various cleaning methods in particular with chemical and mechanical have been the most popular.

This is not a surprise, and indeed very regrettable since cleaning is a major concern for terra cotta building and is not a one-time operation. Consequently, attention to the substrate, color changes, and pH changes on the surface should be recorded before and after treatment in order to correctly assess and evaluate the cleaning methods, and consequently learn from for future treatments. (Matteini, 2014).

3. METHODOLOGY

After completing the literature review, the second part of this research focused on the assessment of the effects of two commercial acid based cleaners on unglazed terra cotta. In the next two chapters, all of these steps are illustrated.

3.1 SAMPLE PREPARATION AND TREATMENT

The samples were generously donated by Boston Valley Terra cotta in Buffalo. The tiles provided were 6”x 6”x½”, unglazed and hand-pressed terra cotta of two different colors: red and tan. For the purpose of our testing, each tile was subsequently cut into 4 smaller samples of 3”x 3”, where each set contained one control and three cohorts. (Appendix 1.0)

The tiles were treated with two different commercial acid based cleaning products in two applications: ProSoco Sure Klean Heavy Duty Restoration Cleaner based on hydrofluoric acid, and ProSoco Enviro Klean Restoration Cleaner based on ammonium bi-fluoride.

For both products, manufacturer’s instructions were followed: Heavy Duty Restoration Cleaner was diluted 1 part cleaner to 3 parts water by volume and applied with a dwell time of 5 minutes, the maximum time recommended by the manufacturer. Enviro Klean Restoration Cleaner was applied as a concentrate, with a dwell time of 20 minutes, the maximum time recommended by the manufacturer.

3.3 WEATHERING TESTING PROTOCOLS

Two testing protocols were selected based on the weathering agents that generally affect the durability of terra cotta, the instrumentation accessible at the Architectural
Conservation Laboratory, and the limited testing time available for this project: RILEM VB Salt Test and ASTM G154:12 Standard Practice for Operating Fluorescent Light Apparatus for UV Exposure of Nonmetallic Materials.

- **RILEM VB SALT TEST**: This test consisted of 15 cycles of 2 hour immersion in a 10% solution of sodium sulfate. For fifteen days, a daily cycle was completed which included: two hours of immersion, followed by 19 hours oven-dried at 60 degree Celsius and then cooling within 3 hours. The test was run on 32 samples: one representative set of 6 cohorts for each product and application. (Fig. 4)

- **QV-LAB WEATHEROMETER ASTM G154-12**: A QV-Lab apparatus was used to complete this test. Samples were alternatively exposed to ultraviolet cycles of 8 hours at 60 degrees Celsius, followed by a condensation cycle of 4 hours at 50 degrees Celsius which included a 25 minute water spray cycle at the beginning of each condensation cycle. This protocol was completed for a total of 1008 hours. (Fig.5)

![Figure 4: Picture taken during the two hours immersion of the samples while performing the salt test.](image-url)
3.4 EVALUATION METHODS

In order to assess and quantify changes, the samples were evaluated before and after running accelerated weathering tests.

3.4.1 Texture Mapping

Camera texture mapping was selected, in order to measure changes in the texture and to determine the surface profile of the tiles.

The equipment used included: a camera stand, two Maglite quartz halogen raking lights set at an angle of 30 degrees within 7 inches distance from the sample and a SLR Camera Nikon 500D. Several camera settings were tried and ultimately an aperture of F/8 with a time 1/60, and 1/40 and ISO 200 were selected. A scale card was placed on the left side of each tile as a reference. (Fig. 6)

After photographing all the samples, the files were opened as raw files in Photoshop CS 6, and then edited: lens correction applied, contrast increased, and image conversion to black.
and white. The use of black and white helped emphasize the surface texture and the profile of each tile. (Fig. 7)

The resolution of the pictures was 300 dpi, with a pixel quantity between 11.6 M - 12.6 M. This technique provided exclusively comparative qualitative data.

Figure 6: Camera station used to take pictures

Figure 7: Early test with texture mapping photography
3.4.2 Scanning Electron Microscope

A total number of 18 samples was analyzed by using the scanning electron microscope, in order to evaluate and assess changes in the morphology and in the pores structure of the tiles. (Fig. 8)

The settings used were: magnification 1000X and 2500X, high-voltage of 20.00 kW, spot area 3, and chamber pressure of 1.00 Torr.

3.4.3 Spectrophotometer

A CM2500D Konica Minolta Spectrophotometer was used to assess any changes in color in all of the 96 tiles before and after running accelerated testing. The reading for each tile was taken in the center of the sample. For each set, the control was used as a target and the cohorts as samples. The data were elaborated by using the C18 Minolta Software before and after accelerated weathering. (Fig. 9)
3.4.4 Liquid Nitrogen Porosity

Liquid Nitrogen was used to measure porosity. This method is based on the liquid immersion technique ASTM C830 and proved useful as applied to cultural material (ceramic sherds) at the University of Las Vegas. (Harry et al., 2004)

Porosity is then calculated as: \( P = \frac{W_D}{W_S} \times 100 \)

The equipment used included: a Sartorius electronic balance with an under-hook, metal wire for hanging the tile, and a Dewar flask for the liquid nitrogen. (Fig. 10)
The liquid nitrogen technique follows under the liquid impregnation method, where open pore volume is determined by calculating the amount of liquid nitrogen adsorbed by the open pores. Several are the advantages of using liquid nitrogen for porosity measurements: it is very affordable, easy and quick to use as well as being more accurate than water based measurements and less toxic than mercury porosimetry. It evacuates on its own, so there is no need to physically remove it from the tile as in the case of mercury, or a need for a vacuum. (Matteini, 2014)

One of the critical aspects of using liquid nitrogen is that it evaporates very rapidly, requiring immediate measurement of the wet weight (W) after removing the tile from the liquid.

4. RESULTS AND CONCLUSIONS

In conclusion, this testing protocol attempted to examine the weathering vulnerability of new commercial unglazed red and tan terra cotta. Several conclusions can be made as a result of our findings. Ammonium Bi-Fluoride, firstly introduced in 2000, was presented as a less aggressive delivery of hydrofluoric acid. Consequently, the samples treated with this product did show a reduced alteration of the microstructure compared to the samples treated with hydrofluoric acid based cleaners. However, the variations in color were significant, which represent an important physical property of terra cotta. This could be attributed to the presence of deposits observed in the tiles after the treatment. By conducting EDS and XRD, these precipitations were identified as calcium fluorides. Further analysis with FTIR should be conducted in order to study the formation of these deposits and their impacts on the terra cotta. (Matteini, 2014)

Indeed, for Hydrofluoric Acid cleaners the case is different. Hydrofluoric acid based cleaners, widely in use since the early 1960’s (Boyer, 2014), showed irreversible changes to the microstructure of the pores as previously observed (Matero et. al, 1996). (Fig. 12) Furthermore, signs of physico-chemical erosion on the samples treated with HF were significant, including increase in surface roughness. No significant color variations were observed on these samples.

Today, the results strongly suggests that the Heavy Duty cleaner based on hydrofluoric acid not only enlarged the pores, but caused the terra cotta to be further altered by the salt crystallization test. This suggests for an increase vulnerability as a result of the cleaning. Conversely, the Enviro
Klean product based on ammonium bi-fluoride neither enlarged the pore structure after cleaning or after the salt crystallization test.

![Figure 11: Red sample treated with one application of HF before and after running the salt test. Changes in the pore structure are visible (Left side magnification 1000X, right side 2500X)](image)

In the end, this research should be continued and extended, and further considerations should be taken:

- Extend to glaze terra cotta sample and possibly to historical samples – For this research, only new unglazed terra cotta samples were used.
- Additional exploration of quantification methods should be done, especially on the study of surface texture change.
• Further analysis of the clay composition of the tiles to better understand the chemistry of the precipitation occurred on the samples treated with ammonium bi-fluoride.
• Freeze-Thaw and longer time for weathering cycles are recommended.

AKNOWLEDGMENT

I would like to thank Prof. Frank Matero and Prof. Reza Vatankhah for their strong support with this research, Boston Valley Terra cotta for providing the samples and making this research possible, David Boyer from ProSoCo for sharing his knowledge and providing the products for the treatment. Thank you to the following institutions: Nanotechnology Center for providing access to the Scanning Electron Microscope, Penn Museum and Marie-Claude Boileau for her assistance with the petrographic analysis and Susan Tunick of Friends of Terra cotta for sharing her collection of American Architectural Terra cotta.

REFERENCE

Atlantic Terra cotta Company 1916. Spring Cleaning, Atlantic Terra cotta Magazine, (3) 8. This publication documents the cleaning of the Woolworth Building in New York; this building was cleaned twice: first in 1916 only three years after its construction and then in 1932 by using a soap wash, Gold Dust with sharp sand. The company recommended cleaning glazed terra cotta with commercial detergents such as Gold Dust or Old Dutch which contained pumicite. Unglazed terra cotta was to be cleaned instead with “a little” muriatic acid (1 qt to 4 gal.).


Ashurst, Nicola 1994. Cleaning historic buildings. Donhead Publishing Ltd. London. In this publication, Ashurst describes the “perceived” large scale damage reported on the Natural History Museum in London, as a result of the misuse of an HF based cleaner (1970’s).

Boyer, David 2014. Personal communication. President CEO of ProSoCo, Inc., Lawrence, Kansas.


Congressional Serial Set 1913. House Documents, Government Printing Office vol.128. Washington, DC. “The sand-blast in America was exhibited at the Philadelphia Centennial in 1876. The past 36 years have been spent in constant effort by the American Manufacturer to demonstrate the adaptability of sand blast to metal and other cleaning, over old methods.”

Dajnowski, Andrzej & Jenkins, Adam, & Lins, Andrew 2009. The use of lasers for cleaning large architectural structures, APT Bulletin, 40(1): 13-23. This publication includes several large
scale projects entirely cleaned with laser. An example for terra cotta is the laser cleaning of the polychrome cornices of terra cotta at the Philadelphia Museum of Art.

Fidler, John 1981. The conservation of architectural terra cotta and faience, ASCHB Transactions 6:3-16.


Glance, Richard A. 1985. Terra cotta: rehabilitation of a courthouse dome. APT Bulletin, 17 (2):39-45. In this case study, wet sandblasting was used to remove multiple coatings from the terra cotta. Ultimately, the glaze was completely removed, and this method dismissed.


Oujjaa, Mohamed & Rebollar, E. & Castillejo, M. & Domingo, C. & Cirujano, C. & Guerra-Librero, F. 2005. Laser cleaning of terra cotta decorations of the portal of Palos of the Cathedral of Seville. *Journal of Cultural Heritage*, 4(6):321-327. This is the first example of a large scale terra cotta cleaning project executed by Q-switched Nd:YAG laser. The cleaning of the terra cotta was completed in two phases: first, a micro-abrasive system was used, followed by the laser. Furthermore, this is one of the only case studies where a chroma-meter was used before and after treatment to determine changes in colour.


Root, John 1885. Architectural Ornamentation. *Inland Architect*, 5(4):55. Root used a deep red colored terra cotta and brick for the exterior of the Rookery (1885) and a white glazed “enamel” brick for the interior courtyard to increase light reflectance.

Rossol, Monona 2014. Personal Communication. Industrial Hygienist, Arts, Crafts & Theatre Safety, New York City, NY. Monona stated: “By the end of 1970’s, the use of chemicals increased exponentially, consequently OSHA and EPA began introducing regulations on the use and disposal of chemicals. In 1972, EPA introduced the Clean Water Act; followed by HAZCOM, OSHA’s first training for handling chemicals in 1994, which became mandatory as of December 2013. Furthermore, by the end of the 1990s, major metropolitan areas started to ban the use of HF cleaning formulations due to the reported damage to adjacent surfaces from wind drift as well as reports of substrate damage”.


Valoria, Ted 2014. Personal communication. Vice-President of Sponge-Jet, Charleston, South Carolina. Valoria stated: “Introduced in 1994, SpongeJet is a micro-abrasive system that uses synthetic sponge-encased media. SpongeJet reported that the number of applications for terra cotta cleaning have increased in the past few years, mainly on the east coast.”


APPENDIX 1.0 SAMPLING

Figure 12: Sample set treated with one application of ProSoCo Heavy Duty Restoration Cleaner.

Figure 13: Sample set treated with two applications of ProSoCo Heavy Duty Restoration Cleaner.
Figure 14: Sample set treated with one application of ProSoCo Enviro Klean Restoration Cleaner

Figure 15: Sample set treated with two applications of ProSoCo Enviro Klean Restoration Cleaner
**Irene Matteini** began her undergraduate studies in Architecture at Politecnico di Torino and completed her Master’s degree in Architecture at the Illinois Institute of Technology in Chicago in 2009. She then worked for Mass Studies in Seoul, South Korea where she gained experience, an understanding and appreciation for emerging cities and architecture of the 21st century. Additionally, she worked with Artgineering, an office based in Rotterdam, The Netherlands. Following these experience, she was invited to become a visiting researcher at IIT, where she taught for a third year undergraduate studio and lectured at the Italian Institute of Culture and at the School of the Art Institute. She developed a strong interest in Architectural Conservation; more specifically, in Preservation of Modern Architecture. She recently completed an MS. in Historic Preservation at the University of Pennsylvania. Currently, Irene is working as a Project Architect / Architectural Conservator at Echem Consultants LLC, a material consultants firm specializing in Concrete and Corrosion Studies.