Final Report

TITLE: Large Metal Artifact Treatment Plan for Fort Sumter National Monument

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Literature Review of Treatment Methods

The conservation of any ferrous metal artifact consists of three distinct phases; assessment of its current state of degradation, selection of the most appropriate treatment and subsequently monitoring the artifact. The assessment of the artifact focuses on both the presence of active corrosion and the potential for active corrosion to occur in the future. If no active corrosion is present or the potential for significant active corrosion is low, then a passive approach involving regular maintenance and the application of a barrier treatment such as a paint may represent the most effective recommended treatment. On the other hand if active corrosion is present and the potential for continued significant activity is also high, a more aggressive treatment strategy may be required.

In the case of most metal artifacts, especially those made of cast or wrought iron; this involves the removal of chloride (Cl^{-1}) ions from the corrosion products and the interfacial regions and the prevention of subsequent active corrosion. This has been the topic of many investigations and remains one of the most active areas in metals conservation research. In addition to its presence as a Fe^{+n} counter-ion in soluble salts, the Cl^{-1} ion containing compounds that have been most often associated with the corrosion of recovered artifacts include β-FeOOH (akaganéite), hydrated ferrous chlorides ($FeCl_2 \cdot 2H_2O$ and $FeCl_2 \cdot 4H_2O$) and green rust (a mixed valence Fe^{+2} and Fe^{+3} hydroxide and oxy-hydroxide) of variable Cl^{-1} content. Of the above compounds most of the attention has been focused on the formation and presence of akaganéite in iron recovered from terrestrial sites and its role in the post excavation corrosion processes that have been observed. Regardless of its source, there can be no argument that the presence of Cl^{-1} plays an important role in both the extent and rate of post-excavation corrosion.

Consequently, any successful conservation of an iron artifact under severe risk must involve the removal of as much Cl^{-1} as possible.

Barrier Treatments

For more than a century, and especially before the role of Cl^{-1} in post excavation corrosion of iron artifacts was fully appreciated, conservators and scientists experimented with treatments designed to prevent archaeological iron from disintegrating before their eyes. In the early years, physical protection was solely used on ancient iron with the intent to create an impermeable barrier to air. Since iron corrodes when exposed to the air it often was assumed that protecting recently excavated artifacts would be just like protecting modern iron. Various substances were utilized such as paint, oil, wax, lacquers, gelatin, vaseline, rubber or resins (Jakobsen, 1988, Häyhä, 2000). Some treatments involved boiling the artifacts in a mixture of wax and linseed oil while others included the use hydrochloric acid and glycerin (Brinch Madsen, 1987). While modern formulations have changed significantly, the role of a barrier coating in preserving an artifact still depends primarily on preventing the transport of moisture to the surface of the metal.

Electrolytic Treatment

A significant step forward in iron conservation history occurred in 1882 when a German scientist, Edward Krause, published an article about the importance of eliminating soluble salts from the metal in order to stabilize it (Krause, 1882). Krause recommended using hot and cold distilled water until no chloride could be detected in the solution. Krause also mentioned that insoluble salts were harmless to the metal. Later references indicate that many of the artifacts conserved by Krause had to be retreated by the turn of the century and very few, if any, survived to the present day (Jakobsen, 1988). Another early turning point occurred in 1892 when Axel

Krefting in Norway published an article on the influence of soluble salts on archaeological iron, and the way to conserve ancient metal artifacts (Krefting, 1892). Krefting, an engineer and amateur archaeologist, made the claim that the only way to get rid of the salts was to strip the corrosion products to the bare metal using a method called "electrolytic de-rusting". He also noted that the best way to achieve this goal was to use a 5% solution of sodium hydroxide. Krefting's technique drew considerable attention due to the relative efficacy of the treatment. However, the technique also was criticized because of the "stripped" appearance of certain artifacts after treatment. In addition, Krefting also recommended the use of paraffin wax to protect the artifacts after treatment. During that period, stripping in acids was very popular along with heating the artifacts, so the approach of using an alkaline solution instead was a departure from normal protocols. While it is difficult to ascertain who was the first "conservator" to use electrolysis in caustic solutions for the stabilization of archaeological iron, one can reasonably assume that Krefting was one of the first. By 1888, Friedrich Rathgen, a scientist hired by the Royal Museums of Berlin already had used this technique on ancient bronze artifacts to stop their alarming corrosion, believed to be due to a fungus. Rathgen had heard about this technique from Adolph Finkener, a chemist at the Bergakademie in Berlin (Gilberg, 1987). The major difference between the process of Krefting and that used by Rathgen was that the electrolyte used by Rathgen was potassium cyanide: a rather dangerous chemical compared to sodium hydroxide. However, it would seem that this method produced reasonably good results and continued to be used for some time on both bronze and iron antiquities (Gilberg, 1987).

Since their initial use electrolytic treatments have remained a subject of discussion and controversy. One of the most striking observations that can be made about the application of electrolytic techniques is the notable lack of consensus amongst its users. This is particularly

true with regard to how to use the technique reliably and effectively on cast iron objects recovered from a marine environment (North, 1977; McCarthy, 2001; Dalard et al, 2002, O'Ginness Carlson, 2003; Mardikian, 2005). Questions about the most suitable electrolyte (e.g. sodium carbonate versus sodium hydroxide), the choice between constant current and potential (Carlin, 2001), and the size, nature and placement of the anodes have yet to be satisfactorily addressed in the literature. A number of scholars also have questioned the role of the electric field in the Cl^{-1} removal process. This point has been the subject of much debate over the years with no definite resolution given to date. North has postulated that the principal effect of electrolysis is the reduction of the corrosion products (due to the increased porosity of the graphite matrix) leading to a faster Cl^{-1} diffusion. Consequently, North and Pearson in 1978 suggested that once the reduction in the corrosion products had occurred, the role of electrolysis should be minimal, and the chloride diffusion in a 2% NaOH solution should constitute the main driving force.

Recent data from experiments designed to compare electrolysis to simple alkaline soaking seem to indicate that the two treatment modes produce essentially the same results on wrought iron in terms of Cl^{-1} extraction rates and residual Cl^{-1} levels in the metal after treatment. A similar trend was found on marine cast iron, although the chloride release appears to be faster in the early stages of the electrolysis on this particular material. This finding seems to confirm North's prediction that once the reduction in the corrosion products has occurred, the role of electrolysis should be minimal and the chloride diffusion in a 2% NaOH solution should constitute the main driving force (Selwyn, 2004). Others have showed that if the gas evolution at the surface of the artifact is too vigorous, the rate of Cl^{-1} released into the solution can be reduced (Carlin, 2001). The relative success of the 'electrolytic reduction' probably can be

explained by the apparent simplicity of the process and the formidable potential it has for cleaning metal surfaces. Unfortunately, along with the possible reduction of the corrosion products and extremely long treatment time (Logan, 1989), the loss of the original surface (particularly on cast iron artifacts) is a significant risk. As noted recently by Dalard, electrochemical stabilization in potentiostatic mode is still a fairly long procedure and often results in weakening the objects due to the difficulty in preventing hydrogen evolution. As a result the materials can end up fracturing during treatment" (Dalard et al, 2002).

In addition, numerous other things can conceivably go wrong with electrolysis, and damage to the fragile graphitized metal can happen in a manner that might not be readily apparent (North, 1975; North 1977; McCarthy, 2001; Dalard et al, 2002; O'Guinness, 2003; Selwyn, 2004; Mardikian, 2005). This statement has proven to be particularly true for large marine artifacts due to their lack of accessibility in the treatment tanks. Consequently, Dalard et al. have suggested using pulsating current techniques to ameliorate the way electrolysis is conducted on marine cast iron.

<u>Alkaline Soaking Treatment</u>

A number of authors have shown that Cl^{-1} can be extracted from archaeological iron by diffusion in caustics without electrolysis or the use of a reducing agent (Pearson, 1987; Keene, 1991; Turgoose et al, 1996; Al-Zahrani, 1999; Gonzalez et al, 2003; Drews et al, 2004; Degrigny, 2004; Selwyn, 2005). Although this technique has given inconsistent results in the past (Pearson, 1987), there now seems to be more evidence that the Cl^{-1} level in deconcreted marine wrought or cast iron can be reduced to a very low limit just by simple diffusion in sodium hydroxide solutions. One notable exception to this observation is the case where β-FeOOH (akaganeite) has formed in the presence of enough soluble Cl^{-1} ions in the corrosion products of

the metal (Drews et al, 2004). This chemical transformation seems to occur only when the metal is exposed to oxygen and to some degree of drying (Gilberg, 1982; Drews et al, 2004).

From a practical standpoint, the presence or absence of this corrosion product might significantly complicate or facilitate the stabilization treatments and explain why certain artifacts become almost impossible to stabilize after they have dried out to some extent. In addition, exposure to the atmosphere and drying can result in the loss of the original surface of the graphitized cast iron when they are placed in NaOH solutions. It is important to note that this kind of adverse reaction is not known to occur on freshly deconcreted marine artifacts.

While it is now believed that the role of NaOH as a chloride extraction media is more significant than originally thought, more work is required to better understand the real nature of the interaction between this chemical and the metal (Selwyn, 2004). For any diffusion technique to work efficiently, the surface of the corroded metal should be as "concretion free" as possible before the treatment starts. The chemical should preferably be circulated and the formation of carbonates prevented. In addition, the electrochemical behavior of the artifact should be regularly monitored along with the pH of the solution. It is also critical to inspect the artifacts on a regular basis during the process. Current research also suggests that NaOH solutions are much more efficient than sodium carbonate solutions for the stabilization of marine iron. However, NaOH solutions are less stable than sodium carbonate solutions probably due to the depletion of OH^- during the exchange with Cl^{-1} and the following reactions that decrease the pH of the solution through direct exposure to the air:

$$CO_{2(g)} + OH^-{}_{(aq)} \leftrightarrow HCO_3^-{}_{(aq)}$$
$$HCO_3^-{}_{(aq)} + OH^-{}_{(aq)} \leftrightarrow CO_3^{-2}{}_{(aq)} + H_2O$$

In his experimental study, (Al-Zahrani, 1999) used a combination of NaOH and de-

aerated nitrogen. Although Al-Zahrani does not explain the technical reason for using an inert gas, it can be assumed that this precaution was used to prevent carbonates from forming and to lower the pH of the solutions, which in turn could play a role in reducing the efficiency of the Cl^{-1} removal process. The inert gas also results in the depletion of oxygen in the solution. As the acidic iron chlorides diffuse out of the artifact it is possible to form a thin layer of relatively low pH at the surface of the artifact. Consequently, even if the bulk solution pH is very high, corrosion could occur at the artifact surface in the presence of O_2. Use of an inert gas to lower the dissolved O_2 concentration in the solution would reduce or eliminate the potential for corrosion to occur in these surface layers.

Reductive Alkaline Treatment

North and Pearson introduced the alkaline sulfite technique in 1975 as an alternative to the electrolytic stabilization of marine archaeological cast iron (North, 1975). This technique became increasingly popular for the stabilization of small terrestrial artifacts. However, its application for large marine artifacts has been very limited. Reasons for that possibly are linked to technical difficulties associated with heating the solution, and the need to use airtight containers to prevent the oxygen from reacting with the chemicals. Although the treatment protocols can vary slightly from one laboratory to another, it would seem that attempts to standardize the technique for terrestrial iron have been relatively successful. In France, for instance, the alkaline sulfite technique has been in use for more than twenty years with reasonably good success for the mass treatment of terrestrial iron artifacts (Loeper-Attia, 1995).

Critical reviews designed to determine the real merit of each technique and evaluate its impact on the survival rate of entire collections of iron artifacts, tend to show that the alkaline sulfite technique remains to date the most successful stabilization treatment available for

terrestrial iron (Keene 1991; Selwyn 1993; Watkinson 1996; Selwyn 2004). This being said, drawbacks to this technique include the potential damage to the surface of certain artifacts, the long treatment time required for their stabilization, the residual sulfates ions remaining in the material, and the problem of determining low levels of chloride ions in the sulfite treatment solutions. More importantly, some authors have shown that a number of terrestrial artifacts treated with alkaline sulfite could not be successfully stabilized with this technique (Beaudoin et al, 1995).

Thermal and Gaseous Reduction Treatments

The idea to thermally treat iron artifacts (annealing) retrieved from a marine environment in order to volatilize the chloride ions has been around for almost 150 years. The earliest reference is cited by Jens Gregers Aagaard describing the work initiated by Mauritz Rasmussen at the Danish Defense Museum in 1858 (Aagaard, 2003). This technique, along with the more elaborate and preferred "hydrogen furnace," also referred to as "gaseous reduction," has been extensively criticized in the conservation literature because of the variability in the results and changes that occur in the iron at such high temperatures (up to 1060°C). Interestingly, thermal treatments have been regularly suggested and tested to stabilize marine artifacts in an attempt to find more reliable and faster conservation techniques. The most recent reference about the continued interest in using annealing to preserve archaeological iron was published in the *Bulletin for the Research in Metal Conservation* # 8 in 2003 (Aagaard, 2003). A modified version of the original "Hydrogen Furnace" treatment was studied at the Western Australian Maritime Museum, Fremantle. Neil North investigated the minimum temperature needed to achieve a good reduction and retain the metallurgical history of the object. A temperature limit of 400°C was found to be an acceptable compromise. Unfortunately, at this temperature, a

subsequent washing in dilute caustic remained necessary in order to diffuse the chloride ions out of the corrosion products. Excellent results were reported on deeply graphitized cast iron cannon balls (North et al, 1976; North, 1977). Recently, the modified hydrogen furnace from the Western Australia Maritime Museum was decommissioned apparently due to Health and Safety rules, not because this technique was considered ineffective (Carpenter, pers. Comm. 2005).

Gas Plasma treatments were introduced in conservation by Daniels et al in 1979 and were further developed in Europe over the last twenty years with mixed results on iron stabilization. The removal of Cl^{-1} from terrestrial iron in alkaline sulfite after a "standard plasma treatment" has been reported to be up to four times faster with this pretreatment than without (Schmidt-Ott, 2002). However, one of the more important technological barriers to the more widespread application of this method is the scale-up factor of going from the small plasma chamber currently being used on archaeological artifacts to a very large chamber. Another technological challenge for the treatment of complex and large artifacts would be the development of a new type of microwave plasma applicator which could be used on the interior and exterior surfaces.

Subcritical Fluids

Prior to the current research at the Warren Lasch Conservation Center, there were no references on the use of super or subcritical fluids for the stabilization of archaeological iron artifacts. This process was based on extensive work with these fluids carried out in the School of Materials Science and Engineering at Clemson University (Drews, Williams et.al., Drews, Barr et.al, 2001). To date, over 60 experiments have been conducted at the Warren Lasch Center on wrought and cast iron samples using subcritical fluid treatment. Although most of the samples which have been treated were from the *Hunley*, two samples were from the Monitor Project and the cast iron samples were from two Civil War era artillery shells that had graphitized layers

~1cm thick. Subcritical water is water maintained at a pressure above atmospheric pressure and $100^{o}C$ and below the critical temperature and pressure of water, Tc =$374^{o}C$, Pc = 220 bar. In the subcritical region, the transport properties of H_2O as a solvent media will be between those of liquid H_2O and supercritical H_2O. The hypothesis was that by using subcritical water solutions, the treatment time would be significantly reduced for the following reasons:

a) The increase in temperature of the treatment solution would result in a significant increase in the Cl^{-1} diffusion constants.

b) The decrease in the viscosity and density of the treatment solution would improve the diffusion of OH^{-} into the corrosion layers and promote a more effective Cl^{-1} anion exchange.

Experiments have been conducted within the temperature range of 130 to $230^{o}C$. These temperatures were selected as representing the best compromise between practical considerations (if a very large artifact was to be treated) and treatment effectiveness. In addition, the pH has been varied from 11.6 to 13.1 and the reactor size increased from 40 to 600 ml. A 35 l reactor, to be constructed in 2006, has been designed for the next phase of the research. In these experiments, the subcritical water treatment effectively has removed very high levels of Cl^{-1} from the samples in very short periods of time. None of the treatments has exceeded 5 days, compared to over 6 months of treatment using traditional techniques on some of the comparative cast iron specimens.

In a very limited set of experiments, simple soaking in NaOH alone was found not to be effective in removing all of the Cl^{-1} present from the metal shavings resulting from the drilling of the rivets of the *Hunley* that had been allowed to completely dry out in air and form akaganeite

(β−FeOOH). This analysis was performed by electron microprobe, micro-Raman analysis, as well as optical microscopy by Dr. Desmond Cook at Old Dominion University, Norfolk, Virginia. In contrast to these results, subcritical treatment of comparative samples has successfully removed all of the Cl^{-1}. More importantly, it was shown that the subcritical treatment resulted in the apparent transformation of β-FeOOH into other iron oxides (Drews et al., in prep). The physical appearance of all the subcritical treated specimens, their mechanical properties, and their apparent corrosion resistance (even those stored in a saturated water vapor chamber for at least 2 years) seems to be very good: so the results from these experiments continue to be extremely encouraging.

Summary

To date, no Cl^{-1} removal technique has yet been demonstrated to be effective in the long run on all kinds of archaeological iron of various sizes and from different burial environments (Knight, 1997; Keene, 1993; Selwyn, 2004; Watkinson 2004; Drews et al 2004). In addition, no conservator can predict with any degree of certainty if a given artifact will remain stable after its conservation is complete unless stored under very controlled conditions such as a relative humidity of 12% or less (Watkinson 2004) or under an oxygen free/low RH system (Mathias 2004, Mardikian 2004). Clearly more work is required to fill the gaps in our current knowledge (Selwyn, 2004). Based on our current state of knowledge, the techniques discussed in the previous sections are compared in Table 1.

Table 1. Synopsis of Treatments

Technique	Required Equipment	Advantages	Disadvantages
Electrolytic	Soaking Tanks Chemical Mixing Chemical Neutralization Powers supplies Reference electrodes Anodes pH and Cl^{-1} analysis	May be more effective than simple soaking for some artifacts	Long treatment times Potentiostats can be relatively expensive Requires constant monitoring May not work for air dried and severely corroded artifacts Generates large quantities of waste water Probability of damage to graphitized layer of cast iron artifacts significant
Simple Alkaline Soak	Soaking tanks Chemical mixing Chemical neutralization pH and Cl^{-1} analysis	Lowest cost Simplest Requires least equipment and technical expertise	Very long treatment times Results are the least predictable May not work for air dried and severely corroded artifacts May generate large quantities of waste water
Alkaline / sulfite	Soaking tanks must be heated and protected from oxygen Chemical mixing Chemical neutralization Ventilation pH and Cl^{-1} analysis	Low cost Simple Requires low level of equipment and technical expertise May be more effective than simple soaking for some artifacts	Long treatment times May not work for air dried and severely corroded artifacts Generates large quantities of waste water Requires closed containers Not well suited for larger artifacts
Thermal and Plasma	High temperature furnace or plasma generators Appropriate treatment gases Safety equipment	May reduce the treatment times significantly for some artifacts	High temperature may effect metallurgy Expensive to run and maintain Possible safety concerns Not well established for large or complex artifacts
Subcritical water solutions	Appropriate pressure vessel Chemical Mixing Chemical Neutralization pH and Cl^{-1} analysis	Very short treatment times Very effective Cl^{-1} removal May be universally applicable Lower volumes of waste solution	Large pressure vessels very expensive Limited data available Currently requires a high level of technical expertise Long term stability of treated artifacts not yet established

Evaluation of the Park's Collection.

The collection was evaluated visually in order to characterize the condition of the artifacts. The survey was done by artifact groupings, following National Park Service storage protocols.

The main focus of the evaluation was to identify signs of active corrosion such as the presence of powdery material or beads of reddish or brown liquid on the surface of the artifact or evidence of spalling or cracking on the artifact's surface. It is recommended that for selected artifacts additional analysis should be carried out to determine the presence or absence of high levels of chloride in highly distressed areas that were identified during the initial evaluation. In some cases this may require selective, discrete invasive sampling of the artifacts.

If the artifact was made of more than a single material, it was specified as a composite artifact, as this will be essential information required if treatment is recommended. The type of material such as Cast Iron (Cast Fe), Wrought Iron (wrought Fe), Bronze or Copper Alloy (Cu Alloy), Lead (Pb) was identified during that survey based on observation and historical records as this will also have a significant effect on any recommended course of active treatment.

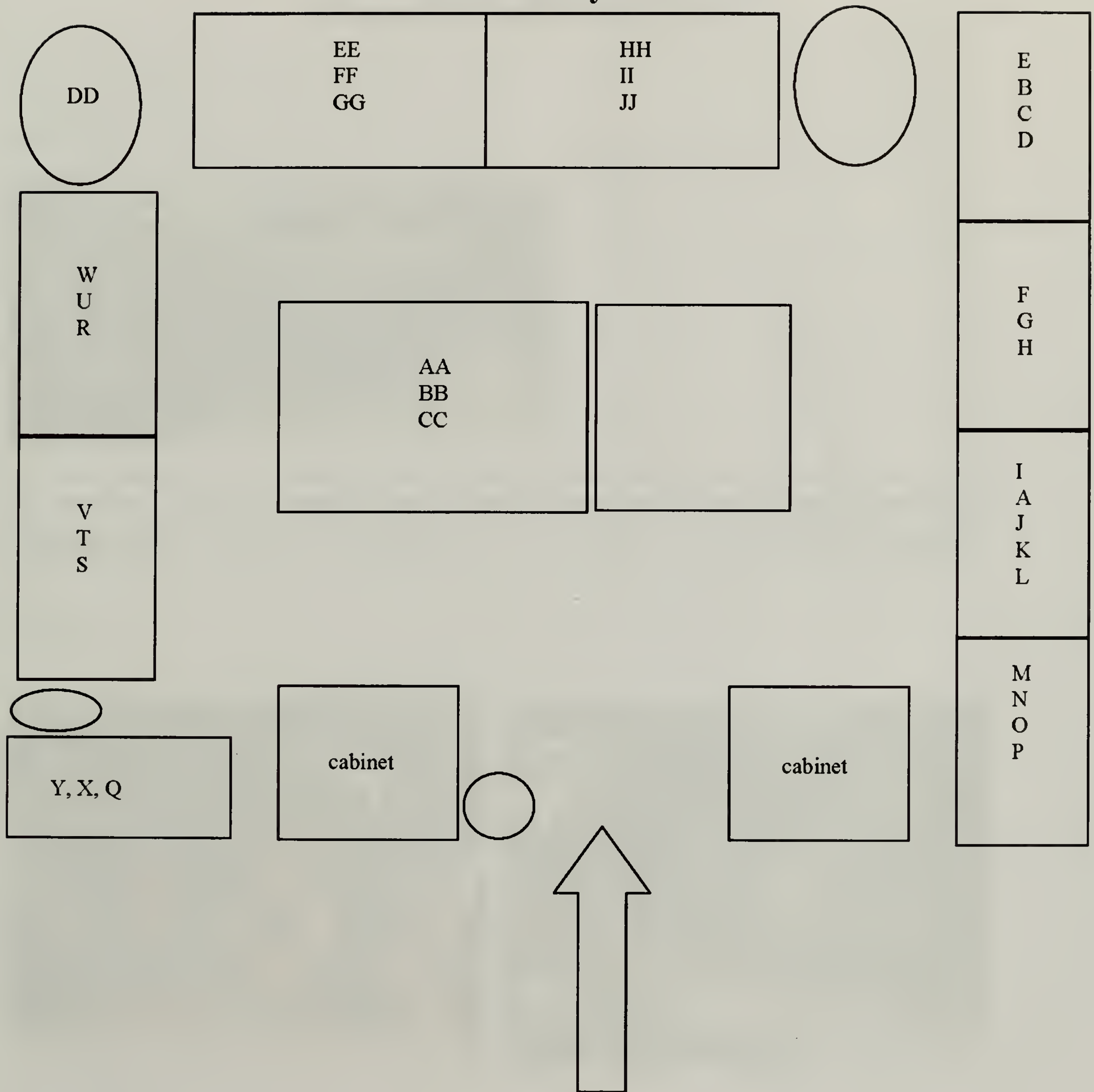
The state of the "original" surface was noted in the survey and classified as either "good" or "poor." "Good" condition indicates that the original surface is primarily intact and present and that the archaeological information is mainly preserved. On the other hand, "poor" condition indicates that a significant fraction of the original surface is missing.

The presence and condition of the paint layer was also noted. Especially in the case of the canons, the integrity of the paint layer was evaluated because of its relevance to the condition of the artifact.

Finally, with regard to the artillery shells an indication was given concerning whether the

artifact was plain or hollow since this would be vital information for any future recommended treatment.

Curatorial Facility Floor Plan



Curatorial Facility Artifacts

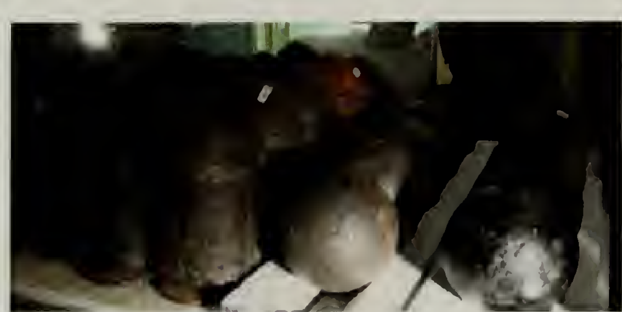
1 Shelf AA

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Musket barrel	No	Steel	Yes	Poor	Hollow

2 Shelf B

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Grape shot	Yes	Wrought Fe + cast Fe	Yes	Good	Solid
Disk for grape shot	No	Wrought Fe	Yes	Good	Solid
Canister disk	No	Cast Fe	Yes	Good	Solid

3 Shelf BB



Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Mullane	No	Cast Fe	No	Good	Solid
Smooth bore	No	Cast Fe	No	Good	Solid

4 Shelf C

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Mullane	No	Cast Fe	No	Good	Solid
Parrott shell	Yes	Pb + cast Fe	Yes	Poor	Hollow

5 Shelf CC

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Carriage wheels	No	Cast Fe	Yes	Poor	Solid
Shells	No	Cast Fe	Yes	Good	Hollow
Shells + sabots	Yes	Pb + cast Fe	Yes	Good	Hollow
Chain	No	Wrought Fe	Yes	Good	Solid

6 Shelf D

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Mullane	Yes	Wrought Fe + cast Fe	Yes	Good	Solid
Exploded shell	No	Cast Fe	Yes	Poor	Solid
20th century shell - 4-7" Armstrong	Yes	Fe + Pb + cu alloy	No	Good	Hollow

7 Shelf DD

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Wheels, gun carrier	Yes	Wood + cast Fe	Yes	Good	Solid

8 Shelf next to D

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Tongue (removed from Parrott gun)	No	Wrought Fe	Yes	Poor	Solid
Armor piercing	No	Steel or cast Fe	No	Good	Solid

9 Shelf E

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Misc.	No	Wrought Fe	No	Misc.	No

10 Shelf EE

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Commemorative plate	No	Cu alloy	No	Good	Solid

11 Shelf F

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Misc.	Yes	Wrought Fe + cast Fe + cu alloy	No	Good	Solid

12 Shelf FF

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Canister for grape shot	Yes	Wrought Fe + cast Fe	Yes	Poor	Solid

13 Shelf G

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Mullane	Yes	Cu alloy + cast Fe	Yes	Good	Solid

14 Shelf GG

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Rifled shell (Parrott + Hotchkis)	No	Pb + cast Fe	Yes	Poor	Mix

15 Shelf H

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Mullane	Yes	Pb + cast Fe	Yes	Poor	Solid

16 Shelf II

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Mullane	No	Cu alloy + cast Fe	No	Good	Solid
Smooth bore	No	Cast Fe	No	Good	Solid
13" mortar shell	No	Cast Fe	No	Good	Hollow

17 Shelf J

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Misc.	Yes	Wrought Fe + cast Fe	Yes	Good	Solid

18 Shelf JJ



Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Parrott shell	Yes	Pb + cast Fe	Yes	Poor	Mix

19 Shelf K

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Mullane	No	Cast Fe	Yes	Good	Solid

20 Shelf L

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Mullane	Yes	Cu alloy + cast Fe	Yes	Good	Solid

21 Shelf N

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Misc. Shells	Yes	Cu alloy + cast Fe	Yes	Poor	Solid

22 Shelf O

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Parrott shell	No	Cast Fe	Yes	Poor	Hollow
Cannon ball	No	Cast Fe	No	Good	Solid

23 Shelf P

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Smooth bore	Yes	Cu alloy + cast Fe	Yes	Good	Hollow

24 Shelf Q

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Smooth bore	No	Cast Fe	Yes	Good	Hollow

25 Shelf R

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Smooth bore	No	Cast Fe	Yes	Good	Solid

26 Shelf S

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Smooth bore	No	Cast Fe	No	Good	Solid

27 Shelf T

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Smooth bore	No	Cast Fe	Yes	Good	Solid

28 Shelf U

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Parrott shell	Yes	Cu alloy + cast Fe	Yes	Good	Hollow
Smooth bore	No	Cast Fe	No	Good	Solid

29 Shelf V

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Misc.	No	Wrought Fe	Yes	Good	Solid

30 Shelf W

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Misc.	No	Wrought Fe	Yes	Poor	?
Misc.	Yes	Cu alloy + cast Fe	Yes	Poor	Solid
Plate	No	Cu alloy	No	Good	Solid
Misc.	No	Cast Fe	Yes	Good	Solid

31 Shelf X

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Misc.	Yes	Wrought Fe + cast Fe + wood	Yes	Poor	Mix

32 Shelf Y

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Misc. Electrical	Yes	Modern materials + Fe	Yes	Good	Mix

33 Shelf next to Y

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
Mortar shell	No	Steel or cast Fe	No	Good	Solid
Armor piercing	No	Steel or cast Fe	No	Good	Solid
Rodman pintle rod	No	Cast Fe (?)	No	Good	Solid
Pintle plate	No	Wrought Fe	Yes	Good	Solid

34 Cardboard box next to the door

x-ray of one grapeshot.

Description	Composite material	Material	Signs of active corrosion in the lot	Condition	Solid/hollow
grapeshot	No	cast Fe	No	Poor	Solid

Fort Sumter Cannons

Note: Artifact IDs are from: The Historic Guns of Forts Sumter and Moultrie" by Mike Ryan, May 1997

1 S-1: 42-pounder, model 1845

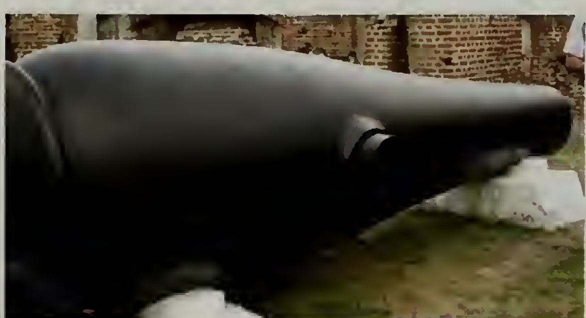
interior of barrell

	EXTERIOR				INTERIOR				
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel	General condition
S-1	No	Yes	Good	Good	No	Partially	Poor	Needs to be cleaned	N/a

2 S-2: 42-pounder, model 1845, rifled & banded

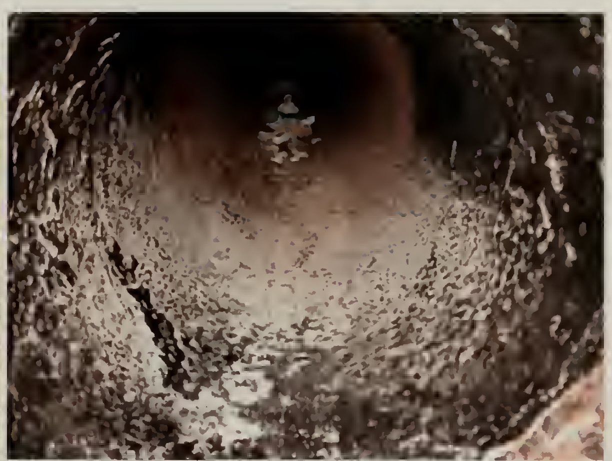
	EXTERIOR				INTERIOR				
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel	General condition
S-2	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	N/a

3 S-3: 15-inch Rodman



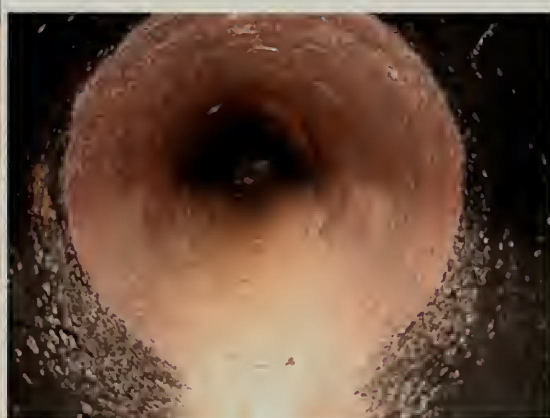
	EXTERIOR				INTERIOR				
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel	General condition
S-3	Yes	Yes	Good	Good	N/a	N/a	N/a	Plugged with concrete	N/a

4 S-4: 8-inch Columbiad, Model 1844



	EXTERIOR				INTERIOR				
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel	General condition
S-4	No	Yes	Good	Good	No	Partially	Good	Needs to be cleaned	N/a

5 S-5: 15-inch Rodman

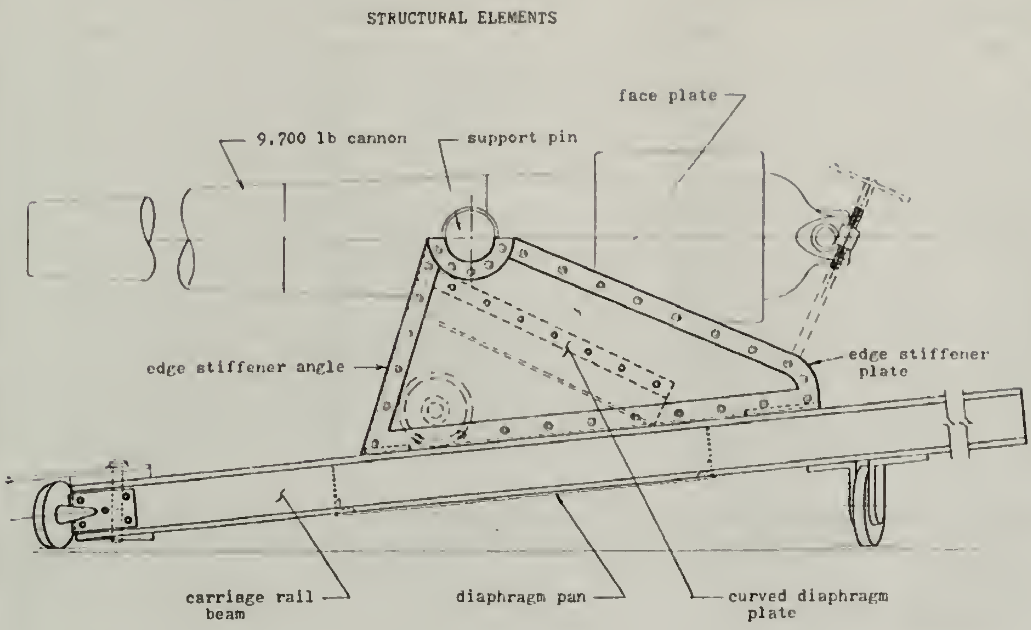


	EXTERIOR				INTERIOR				
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel	General condition
S-5	No	Yes	Good	Good	No	Partially	Good	Needs to be cleaned	N/a

6 S-6: 10-inch Seacoast Mortar, c.1807

	EXTERIOR				INTERIOR				
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel	General condition
S-6	Yes	Yes	Good	Good	Yes	Partially	Good	Needs to be cleaned	N/a

7 S-7 to S-17: 100-pounder Parrott



	EXTERIOR				INTERIOR				
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel	General condition
S-7	No	Yes	Good	Good	No	No	n/a	Needs to be cleaned	N/a
S-8	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Poor
S-9	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Good
S-10	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Good
S-11	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Good
S-12	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Good
S-13	Yes	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Good
S-14	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Poor
S-15	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Poor
S-16	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Poor
S-17	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Poor

	CARRIAGES			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition
S-7	No	Yes	Good	Good
S-8	Yes	Yes	Intermediate	Good
S-9	Yes	Yes	Intermediate	Good
S-10	Yes	Yes	Intermediate	Good
S-11	Yes	Yes	Intermediate	Good
S-12	Yes	Yes	Poor	Good
S-13	Yes	Yes	Poor	Poor
S-14	Yes	Yes	Poor	Good
S-15	Yes	Yes	Poor	Good
S-16	Yes	Yes	Poor	Good

[1] Technical drawing from: *A Report On Nondestructive Testing And Structural Analysis On Eleven Iron Casemate Carriages And Chassis At Fort Sumter National Monument*. Fort Sumter Library

Details of Active Corrosion

Figure 1: detail of carriage from S-13

Figure 2: detail of carriage from S-13

Figure 3: detail of carriage from S-13

Figure 4: detail of cannon S-13

Figure 5: detail of barrel S-16

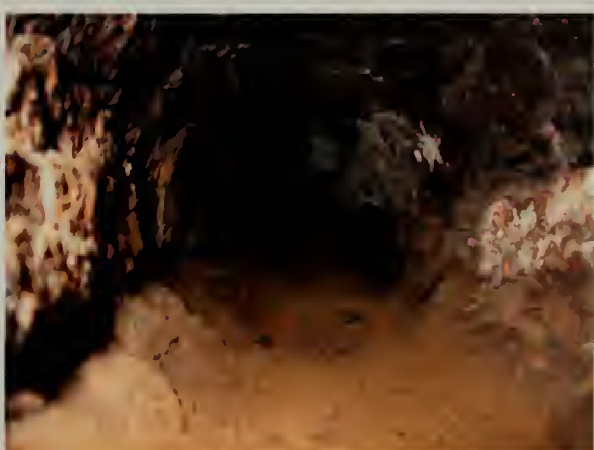


Figure 6: detail of barrel S-15

8 S-18: 10-inch Columbiad, Model 1844, rifled & banded

	EXTERIOR				INTERIOR				
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel	General condition
S-18	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Interm.

9 S-19: 8-inch Parrott

	EXTERIOR				INTERIOR				
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel	General condition
S-19	No	Yes	Good	Good	Yes	Partially	Poor	Needs to be cleaned	Poor

10 S-20: 12-pounder Mountain Howitzer, Model 1835 (Not on display, no evaluation done)

Fort Moultrie Cannons

1 M-1: 10-inch Parrott


	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-1	No	Yes	Good	Good	No	Partially	Good	Needs to be cleaned

2 M-2: 8-inch Parrott


	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-2	No	Yes	Good	Good	No	Partially	Good	Needs to be cleaned

3 M-3: 7-inch triple-banded Brooke

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-3	No	Yes	Good	Good	N/a	N/a	N/a	Plugged with wood

4 M-4: 10-inch Columbiad, Model 1844, rifled & banded

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-4	Yes	Yes	Good	Good	No	Partially	Good	Needs to be cleaned

5 M-5: 10-inch Rodman

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-5	No	Yes	Good	Good	No	Partially	Good	Needs to be cleaned

6 M-6: 10-inch Rodman

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-6	No	Yes	Good	Good	No	Partially	Good	Needs to be cleaned

7 M-7: 10-inch Confederate Columbiad

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-7	No	Yes	Good	Good	No	Partially	Good	Needs to be cleaned

8 M-8: 13-inch Seacost Mortar, Model 1861

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-8	Yes	Yes	Good	Good	Yes	Partially	Good	Needs to be cleaned

9 M-9: 15-inch Rodman

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-9	No	Yes	Good	Good	No	Partially	Good	Plug

10 M-10: 15-inch Rodman

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-10	No	Yes	Good	Good	No	Partially	Good	Plug

11 M-11: 8-inch Columbiad, "new pattern," rifled & banded

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-11	Yes	Yes	Poor	Good	Yes	Partially	Poor	Needs to be cleaned

12 M-12: 10-inch Confederate Columbiad

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-12	No	Yes	Poor	Good	Yes	Partially	Poor	Needs to be cleaned

13 M-13: 32-pounder, Model 1829

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-13	No	Yes	Poor	Good	Yes	Partially	Poor	Needs to be cleaned

14 M-14: 32-pounder, Model 1829

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-14	No	Yes	Poor	Good	Yes	Partially	Poor	Needs to be cleaned

15 M-15: 24-pounder, Model 1819

	EXTERIOR				INTERIOR			
Artifact ID	Signs of active corrosion	Painted	Condition of the paint layer	General condition	Signs of active corrosion	Painted	Condition of the paint layer	Barrel
M-15	No	Yes	Good	Good	N/a	N/a	N/a	Plugged

Capability to Implement a Treatment Program

In this section, two traditional approaches to treating non-composite cast iron were considered; soaking in caustic, and soaking in caustic with electrolysis. It was assumed that with the appropriate additional professional staff, facilities and resources it would be possible to carry out these treatments at any of the three National Parks Services facilities containing the collections: Fort Sumter, Fort Moultrie and the curatorial facility. It should be emphasized that successful treatment requires controlled conditions: temperature, ventilation, spill containment, and waste water disposal. The approach taken in this evaluation was to consider the list of materials and quantities of chemicals required to treat selected, representative artifacts from the collections,

The list of materials below is based on the two most significant groups of artifacts in the collection: shells and cannons. It enumerates the basic equipment and chemicals required to treat non-composite cast iron artifacts, using either soaking in sodium hydroxide or soaking with electrolysis. This list does not take into account the preparation of the artifacts for the treatment (removal of coatings, cleaning, etc.) or post treatment interventions (paint, coating with wax, storage conditions, etc.)

Soaking in Caustic - Shells

(Considering a spherical cast iron shell of 15 inches diameter as a reference)

- Lifting device
- Reference electrode and voltmeter.
- pH electrode.
- Tank (l=1.2m, w=1.2m, h=1.2m)
- Tank cover
- Mixing pump (bulk of solution)
- PVC hose
- Soaking solutions (1% w/w NaOH solution, calculated for 5 changes):
  - tap water: 5.6 m^3
  - DI water: 1.4 m^3
  - NaOH 50%: 144 kg
- Rinsing (DI water: 4.3 m^3, 3 rinses)
- Neutralization of soaking solutions (H_2SO_4 Technical grade, 186 kg)
- Plastic net to support graphite layer
- Analysis of Cl^{-1} in soaking solution (once a month)
- Analysis of Cl^{-1} in the metal.
- Personal protection (boots, tyvek coveralls, goggles)

Soaking in Caustic - Cannons

(Considering a 100-pounder Parrott as a reference)

- Crane and slings
- Reference electrode and voltmeter.
- pH electrode.
- Steel tank (l=4.8m, w=1.4m, h=1.5m)
- Slings for support
- Tank cover
- Mixing pump (bulk of solution + interior of the cannon)
- PVC hose
- Soaking solutions (1% w/w NaOH solution, calculated for 5 changes):

  tap water: 35.0 m^3

  DI water: 8.7 m^3

  NaOH 50%: 874 kg
- Rinsing (DI water: 17.5 m^3, 3 rinses)
- Neutralization of soaking solutions (H_2SO_4 Technical grade, 564 kg)
- Plastic net to support graphite layer
- Analysis of Cl^{-1} in soaking solution (once a month)
- Analysis of Cl^{-1} in the metal.
- Personal protection (boots, tyvek coveralls, goggles)

Soaking in Caustic - Shells

(Considering a spherical cast iron shell of 15 inches diameter as a reference)

- Lifting device
- Reference electrodes (x2) and voltmeter.
- pH electrode.
- Power supply (potentiostat, up to 2 Amp)
- Titanium anodes (4m)
- PVC pipe (to protect anode)
- Isolated cooper wire (10m)
- Tank (l=1.2m, w=1.2m, h=1.2m)
- Tank cover
- Mixing pump (bulk of solution)
- PVC hose
- Soaking solutions (1% w/w NaOH solution, calculated for 5 changes):

  tap water: 5.6 m^3

  DI water: 1.4 m^3

  NaOH 50%: 144 kg

- Rinsing (DI water: 4.3 m^3, 3 rinses)
- Neutralization of soaking solutions (H_2SO_4 Technical grade, 186 kg)
- Plastic net to support graphite layer
- Analysis of Cl^{-1} in soaking solution (once a month)
- Analysis of Cl^{-1} in the metal.
- Personal protection (boots, tyvek coveralls, goggles)

Soaking in Caustic - Cannons

(Considering a 100-pounder Parrott as a reference)

- Crane and slings
- Reference electrodes (x2) and voltmeter.
- pH electrode.
- Power supply (potentiostat, up to 5 Amp)
- Titanium anodes (20m)
- PVC pipe (to protect anode)
- Isolated cooper wire (50m)
- Steel tank (l=4.8m, w=1.4m, h=1.5m)
- Slings for support
- Tank cover
- Mixing pump (bulk of solution + interior of the cannon)
- PVC hose
- Soaking solutions (1% w/w NaOH solution, calculated for 5 changes):
  tap water: 35.0 m^3
  DI water: 8.7 m^3
  NaOH 50%: 874 kg
- Rinsing (DI water: 17.5 m^3, 3 rinses)
- Neutralization of soaking solutions (H_2SO_4 Technical grade, 564 kg)
- Plastic net to support graphite layer
- Analysis of Cl^{-1} in soaking solution (once a month)
- Analysis of Cl^{-1} in the metal.
- Personal protection (boots, tyvek coveralls, goggles)

Recommended Treatment

1. What is Active Corrosion?

Active corrosion is an important "conservation notion" describing the process by which a complex corrosion cycle can occur on iron-based artifacts that have been exposed to enough moisture and chloride ions during their history. Most of the iron artifacts made of cast or wrought iron that have been excavated from marine or terrestrial sites or have been exposed to a saline environment are prone to develop this type of corrosion. These reactions are known to start shortly after the artifacts have been excavated and will proceed as long as oxygen, moisture, chloride ions and iron can react together. The aggravating factor is that certain metal oxides are known to expand up to 3 times in volume during this process damaging or destroying tons of iron every year. This cycle can lead to the alteration of metal surfaces and loss of tool marks, inscriptions and decoration or even to the complete destruction of historical iron artifacts that may have been preserved for hundreds of years during their burial. Under film contaminants such as chloride ions have the ability to modify the adhesion of a protective film (barrier paint) and induce a premature paint failure and localized corrosion. Blistering and coating failure are commonly seen on artifacts and structures in the presence of active corrosion.

2. How to recognize the most alarming signs of Active Corrosion?

"Signs of active corrosion include spalling, cracking, powdery material or loose flakes of rust surrounding an object, reddish-brown or bright orange corrosion at places of fractures where the corrosion has lifted off the underlying metal, and beads of liquid on the surface of an artifact"(Selwyn, 1999 p. 4)

3. Recommendation

a) Type 1: active corrosion

MITIGATION MEASURES:

1. Reduce the relative humidity (RH) as low as possible (desiccation): the environment in which museum objects are stored and exhibited determines their longevity. In the particular case of outdoor collection such as the Fort Sumter NPS this cannot be implemented unless artifacts are located in a controlled environment. One exception to this rule could be the interior of the cannon barrels, which possibly could be sealed off with the appropriate quantity of desiccant. When feasible, reducing the relative humidity under 50% will significantly slow down corrosion reactions. However, it has been shown that in presence of certain corrosion products, the RH should be reduced down to 12% in order to stop the corrosion of iron (Watkinson, 2004 p.98). "When compared to chloride removal treatments for corroded iron, desiccation can now offer greater predictability" (Watkinson, 2004 p.100).

2. Bag the artifacts with oxygen scavengers: according to Turgoose (1982), the corrosion rate for an iron artifact, even in the presence of moisture, should theoretically be reduced to near zero in an oxygen-free environment. The underlying principle of this statement is that in the absence of oxygen corrosion cannot occur. This option is valid

for small indoor artifacts that cannot be stored or treated by other means.

3. Remove enough Cl^- via a stabilization treatment and apply a proper corrosion inhibitor and barrier coating: in the particular case of artifacts that have been excavated and exposed to air, there seem to be no definite and completely successful way to stabilize them. At best, available treatments should be considered as a “stability enhancers” by the means of a reduction of the soluble salts inside the material. Based on the best of our knowledge, complete extraction of both species (soluble and insoluble salts) is not possible using traditional techniques. It appears that passive soaking of an artifact can remove a significant quantity of residual chloride with a minimum of risk. However, terrestrial or marine artifacts that have been exposed to the atmosphere can sometime lose their original surface when placed in sodium hydroxide solutions. This phenomenon is especially true of graphitized cast iron objects. Significantly, this form of adverse reaction does not appear to occur on freshly deconcreted marine artifacts. As a consequence, it would be necessary that any artifacts considered for treatment in caustics be covered with a safety net to retain any surface details during stabilization treatment. Very importantly, any stabilization treatment should include the use of an appropriate corrosion inhibitor and barrier coating. Developing a new methodology and technique to stabilize that category of artifacts would be necessary before treating this collection. Researching the use of alternative electrolytes for the passive stabilization of unstable iron should be a priority.

4. Correct adverse conditions (location, position etc.).

5. Combination of all the above: a successful conservation strategy will incorporate all the possible ways to enhance the long-term stability of the collection.

b) <u>Type 2: no sign of active corrosion (based on visual assessment)</u>

1. Implement a Preventive Conservation Maintenance Plan based on the Code of Ethics and Guidelines for Practice of the American Institute for conservation. http://aic.stanford.edu/pubs/ethics.html

5. Working with park staff, develop the criteria to use to establish the order of artifact treatment in priority order

The criteria used to establish the order of artifact treatment (Priority Order) should be based on:

a) The presence of active corrosion
b) The Historical significance of the artifact

ARTIFACT COMPOSITION

Iron artifacts containing materials other than cast or wrought iron must be classified as "composite artifacts". The presence of lead or copper based jackets or belts or sabots or fuses for instance will necessitate the implementation of a specific treatment protocol or the disassembly of these materials from the shell.

RISKS ASSOCIATED TO CAUSTIC TREATMENT OF DRIED IRON ARTIFACTS
Based on the current research and available data, if an artifact is exposed to the atmosphere and dries, it can lose its original surface when placed in sodium hydroxide. This phenomenon is especially true of graphitized cast iron objects. Significantly, this form of adverse reaction does not appear to occur on freshly deconcreted marine artifacts. As a consequence, based on the current knowledge that we have, it would be necessary that any artifacts considered for treatment in caustics be covered with a safety net to retain any surface details during stabilization treatment.

Recommendation

Developing a new methodology and technique to stabilize that category of artifacts would be necessary before treating this collection. Researching the use of alternative electrolytes for the passive stabilization of unstable iron as well as new soaking protocols (gradual increase in pH) should be a priority.

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