The Subcritical Mass-Treatment of a Range of Iron Artifacts from Varying Contexts

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Abstract

The use of subcritical fluids for the treatment of archaeological and marine archaeological iron artifacts has been under experimentation at the Clemson University's Warren Lasch Conservation Center (WLCC) since 2003 and has shown promise of providing solutions to some of the issues related to the more traditional desalination treatments: Treatment times are but a fraction of those required by the soaking methods; chloride readings are brought to near-negligible levels; desalination can be carried out with or without prior deconcretion; solutions are maintained in sealed containers for the duration of the treatments; and positive results have been seen so far with tests for long-term stability of treated artifacts. Particularly remarkable has been the effect the process appears to have had on corrosion matrices containing the chloride-hosting iron oxyhydroxide, Akagenéite (β-FeOOH) on artifacts that have been allowed to dry out. Results have shown a significant reduction in the quantities of this phase – often linked to the continuation of active corrosion processes within iron artifacts – through transformation into more stable corrosion products such as magnetite and hematite. Experiments carried out to date have not only involved single samples and artifacts, but testing has progressed to a stage where numerous artifacts have been successfully stabilized simultaneously in the same batch. The work presented describes three of such desalination treatments. The first run included a single wrought iron ballast block from the H.L. Hunley, a confederate Civil War submarine lost in battle in 1864. This was followed by the first batch run on five similar ballast blocks and a second with nine iron artifacts of varying composition, context and condition, selected from the National Park Service (NPS - USA) curatorial collection.

Introduction

After extensive studies and testing for 9 years at the WLCC, the subcritical treatment has proven to be an effective alternative for the stabilization of iron and iron corrosion products of materials recovered from marine and terrestrial contexts.

In order to stabilize the iron matrix, the presence of chloride ion (Cl^-), often linked to active corrosion processes must be eliminated or rendered inactive (deViviés, *et al.* 2007: 26-30; Drews, *et al.* 2004: 247-260; González, *et al.* 2007: 32-37).

The desalination treatments used in the conservation field are based on the exchange of Cl^- with hydroxide ions (OH^-). Therefore, the solution carrying the OH^- must reach the sites where the Cl^- are located, which often means penetrating through pores and interstices following paths with high degrees of tortuosity through corrosion layers and concretion (Selwyn 2004:294-306; Selwyn, *et al.* 2001:109-120; Selwyn, *et al.* 1999:217-232). Once the chloride sites are reached, an excess of hydroxide is necessary in order to facilitate the exchange. Then, the newly released Cl^- must diffuse out through the material towards the bulk of the treatment solution. In the atmospheric region these processes are slow and their end point is often difficult to determine. Traditional desalination techniques rely on diffusion, which is based on concentration gradients that are significantly affected by the presence of any type of material that may act as a membrane such as corrosion layers and concretion.

The most appealing reason to consider working in the subcritical region is that the properties of water are tunable by simply adjusting the temperature and pressure of the system. Changes in temperature and pressure can provide new thermodynamic and kinetic options, or chemical paths, not viable at lower temperatures.

The subcritical metal treatment developed at the WLCC utilizes alkaline solutions at temperatures and pressure above 100℃ and 30bar, respectively (Drews, *et al.* 2011). To date more than 130 experiments have been performed to evaluate the effects of subcritical treatment on a variety of archaeological wrought and cast-iron samples from both terrestrial and marine sites (deViviés, *et al.* 2007: 26-30; Drews, *et al.* 2004:247-260; Drews, *et al.* 2011; Drews, *et al.* 2005:77; González-Pereyra, *et al.* 2010:39-49; Mardikian, *et al.* 2006:82-88). Based on the results, the subcritical treatment has demonstrated to be effective, safe and exceptionally fast in removing chloride (deViviés, *et al.* 2007:26-30; Drews, *et al.* 2004:247-260; González-Pereyra*, et al.* 2010:39-49).

This paper discusses three recent treatments using subcritical fluids, with specific emphasis on the benefits this technology may offer to the mass treatments of collections of metallic cultural heritage. Amount of Cl^- released during treatment as well as corrosion products and elemental compositions of the various artifacts were monitored using ion chromatography, X-ray Fluorescence, micro-Raman, and SEM-EDS.

Subcritical Technique

Throughout this paper, the region where water remains in the liquid phase and extends from its normal boiling point (100ºC, 1bar) to its critical point (T_c = 373.9ºC, P_c = 220bar) will be referred to as *subcritical region*, while the region under 100ºC, at normal pressure, as *atmospheric region*, as illustrated in Figure 1a. In the sub-critical region there is a significant departure of thermodynamic, transport and chemical properties of water from those at normal conditions, redefining water as a reaction medium. Viscosity, surface tension and density all decrease for pure water or a dilute water solution including the 0.5w% sodium hydroxide (NaOH). Density, probably the most defining thermodynamic property, is affected by temperature. At high temperatures liquid water expands considerably decreasing its density. Many properties of water are affected by this change, in particular the behavior of water as a solvent (Fernández-Prini, *et al.* 2004). Viscosity and surface tension are also affected. They decrease as the temperature increases, resulting in enhanced wetting properties and higher ability to penetrate pores or interstices. An increase in the diffusion constants for Cl^- and OH^- of about 9% will also occur, relative to the diffusion constants at 25^{o}C and 1bar when the temperature and pressure are increased to approximately 180^{o}C and 50bar, respectively (Bird, *et al.* 1992).

The subcritical region also allows the use of NaOH at concentrations that are lower than what is common with traditional treatments, thus easing the burden imposed by its disposal. Additionally, evidence suggests this process also results in the transformation of certain iron corrosion products into more stable phases (akaganéite and lepidocrocite transform into hematite) (deViviés, *et al.* 2007:26-30; González-Pereyra, *et al.* 2010:39-49).

An additional promising characteristic of this alternative treatment is the short treatment times required compared to traditional techniques (chemical, electrochemical or gaseous). Average treatment periods typically fall within fifteen days. Moreover, this technique provides the potential ability to permeate thick concreted and corroded layers which in theory means that iron artifacts may be pre-treated or even stabilized with subcritical fluids, prior to deconcretion or cleaning (González-Pereyra, *et al.* 2010:39-49). This attribute is of particular interest in the case of terrestrial artifacts that are often too fragile to be cleaned prior to desalination. As such, they often require the addition of a stabilizing consolidant; however this material is likely to interfere with the extraction of the salts. Therefore, subcritical treatment offers the ability to effectively stabilize the residual metal core while the object is still embedded in its concretion.

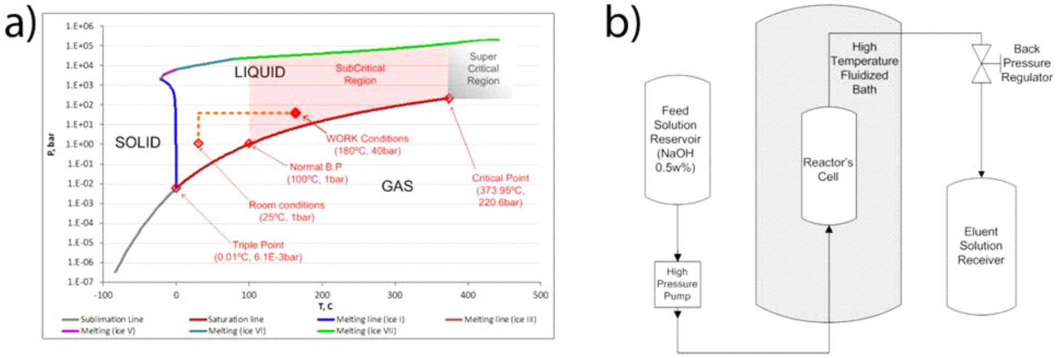

Figure 1: a. Phase diagram for water b. Schematic diagram showing the subcritical reactor system

Subcritical Protocol

The schematic diagram depicted in Figure 1b provides the basic elements of the system. It consists essentially of a feed solution reservoir, a high-pressure pump, a treatment cell, a back-pressure regulator to control the system pressure and an eluent collection vessel. Artifacts are placed in the cell and the fluid flow path primed to flush any air out of the system. Next, the system is closed, brought under pressure, the flow is stabilized and the temperature is increased to the set point. Pressure, temperature and flow of the system are monitored using a computer system. Once the system is running, the eluent is sampled periodically and the Cl^- concentration is measure at the exit of the cell and in the collection vessel by ion chromatography. When it reaches the level of the feed solution, considered the baseline in Cl^- content for ion chromatography, the temperature is turned off and the high-pressure cell is cooled down; the flow of eluent is allowed to continue throughout the cooling process. Once the cell reaches room temperature, the high-pressure pump is turned off and the cell opened to retrieve the desalinated specimen. This latter is then rinsed thoroughly with deionized water and dried quickly to prevent any potential flash corrosion.

The Artifacts

The Ballast Block “Pioneer”

The very first treated artifact utilizing the 40L chamber was a wrought iron ballast block – one of 97 excavated from the *H.L. Hunley*. Apart from a select few of such blocks, having undergone other means of desalination, the majority of these blocks remain stored together in a very large tank of NaOH 1.0w%. The selected block to undergo subcritical treatment was stored separately for several weeks immersed in a pre-treatment solution of NaOH 0.5w%. Thorough documentation and analysis pre- and post-subcritical treatment were performed, as shown in Figure 2. The artifact record showed that partial deconcretion had been carried out prior to immersion in the storage solution to enhance desalination. However the pre-treatment assessment clearly showed some considerable remains of corrosion products, sediment and marine fauna on the surface, particularly within the fine detail. Some mechanical damage to the original surface of the artifact was also noted, where areas of several centimeters were missing, leaving the wrought iron core exposed. It is important to also note the ballast blocks discussed here had never been allowed to dry out and hence no akagenéite was found prior to treatment.

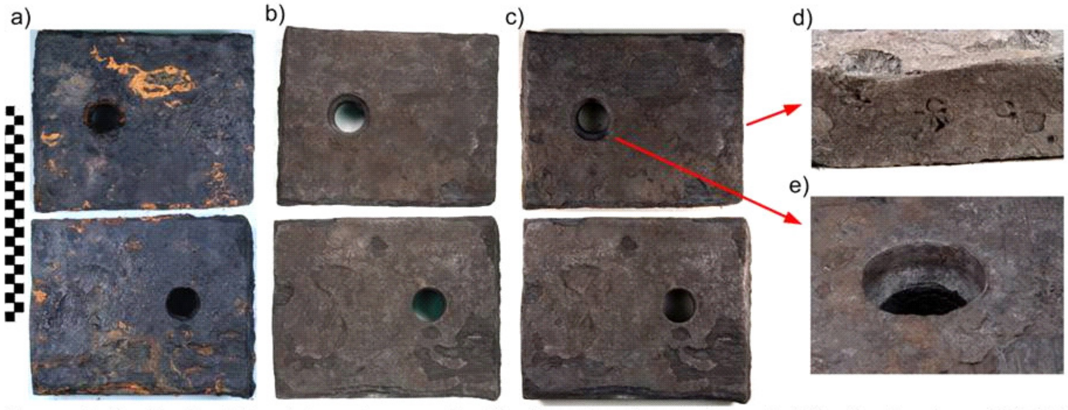

Figure 2: First ballast block to undergo subcritical treatment. a. before stabilization treatment (10/2009), b. immediately after stabilization, drying and cleaning (11/2009) c. condition after nearly 2 years exposed to varying storage conditions (08/2011)

The Five to Follow

Following successful completion of the single ballast block treatment a similar outcome was attempted with multiple artifacts similar in nature. Five further ballast blocks were selected for simultaneous treatment within the 40L chamber. Whilst the artifacts are primarily of the same composition each held very distinct individual characteristics. All had undergone partial deconcretion in the wet state prior to immersion in the above mentioned storage solution, and thus some damage to the original surface had occurred in varying degrees from one block to another.

The National Nine

The following batch of artifacts consisted of nine iron artifacts from the NPS collection. These were of both, wrought and cast iron, consisting of various parts in some examples and from a range of contexts. One common factor for the selection was concern over the stability of the items. All artifacts had been allowed to dry, had been stored in largely uncontrolled environments and thus displaying clear signs of active corrosion in the form of bright orange powdery corrosion products - commonly within pits - as well as blistering, spalling and cracking in some areas of the original surface. Figure 3 illustrates the condition of four of the artifacts prior to subcritical treatment. These artifacts will act as primary examples throughout the paper, as this particular selection received a so-called ‘full conservation treatment’, and were selected as such due to a more prominent surface detail or complex multiple-part features. Out of the selected four, the ring-peg and hinge showed the most structural complexity with moving components and the presence of threaded bolt and nut assemblies. Complex artifacts such as these have commonly posed additional conservation challenges with regards to desalination due to limited permeability of the wash solution into the joins and crevices of such areas, as well as differential corrosion cells at peripheral regions with varying exposure to the environment. It should also be stated that some of the artifacts appeared to have been treated with a penetrating oil-type substance, but no conclusions as to the composition of the product were found in previous treatment records, or through analytical means. The artifacts had also been labeled with catalog numbers applied in black ink over a white label painted directly on to the surface of the artifact.

Documentation and Analysis

All artifacts were systematically assessed through documentation and digital images to identify signs of corrosion. A set of non-destructive characterization equipment was utilized to determine the Cl^- concentration, as well as to identify corrosion products. A FujiFilm NDE DynamIX™ IV *digital radiography system* was used to determine the overall integrity of the object. Corrosion products present on the artifact surfaces were analyzed with a Bruker Optics SENTERRA *micro-Raman spectrometer*. Raman data collection and processing was performed using Opus Version 6.5 software.

The Cl^- concentrations released during desalination was measured by two methods. *Chloride Quan Tab® test strips*, manufactured by Hach® (Loveland, CO), were used to quickly determine quantitative amounts of Cl^- present. *Ion chromatography* was performed using an ICS-90 ion chromatography system with a IonPac® AS9-HC analytical column, both manufactured by Dionex (Sunnyvale, CA). The data was collected and analyzed using the Dionex Chromeleon™ software.

Quantitative and qualitative elemental compositions were determined by an Oxford INCAx-act analytical silicon drift *energy dispersive spectroscopy* (EDS) fitted onto a Hitachi S-3700N Ultra Large VP-SEM *variable pressure scanning electron microscope*. Data collected was analyzed with the INCAEnergy software interface. Qualitative and semi-quantitative elemental analysis was also attained with a Bruker handheld Tracer III-SD *X-Ray Fluorescence spectrometer.*

All results were averaged from at least three data collections.

Results and Discussion

Alongside the evident advantages regarding stability and length of treatment, post-stabilization deconcretion stands out crucially in the eyes of the conservator. The effectiveness of the process allows for drying to take place prior to any mechanical cleaning due to the inherent post-treatment stability of the artifact and its corrosion matrix. This further allows for better and easier visual identification of the corrosion layers and original surface and thus more control over any removal. Full documentation can be carried out after drying with no time limitations due to the threat of flash corrosion or stresses caused by recrystallization.

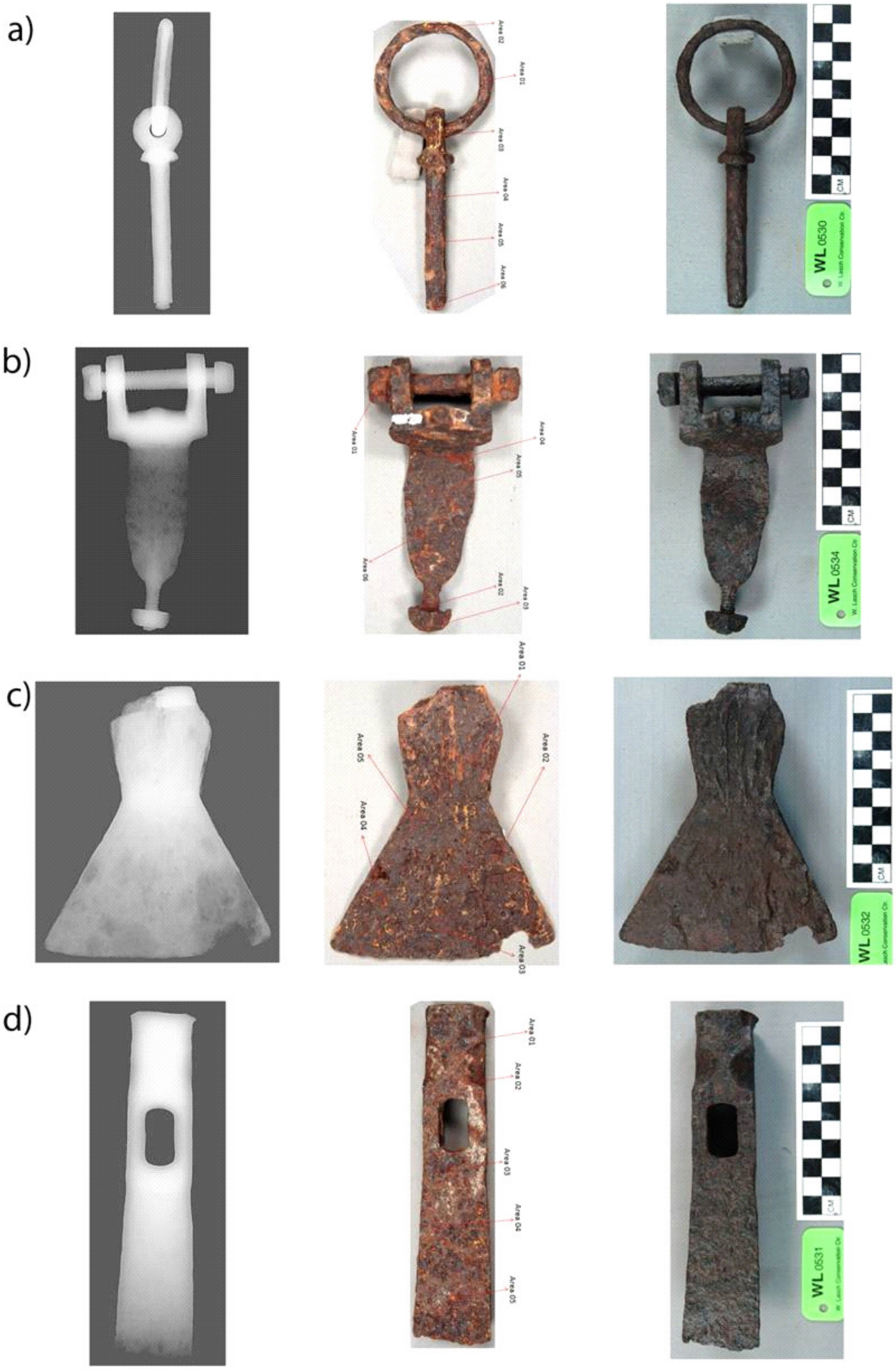

Figure 3: Four of the NPS artifacts: a. ring-peg b. hinge c. axe blade and d. adze/pick. From left to right: X-radiograph; condition before stabilization with areas selected for micro-Raman Spectroscopy and, after completion of full conservation treatment

Ballast Blocks

With regards to the overall appearance of the artifacts, there was very little change with any of the ballast blocks on initial inspection. The first ballast block was stabilized in 16 days. Approximately 90% of the total Cl^- released occurred within the first 5 days, with a maximum peak reached on the first day. Furthermore, after the fifth day the concentration of Cl^- remained under 1ppm. At the end of the run the total amount of Cl^- extracted from the artifact was 0.031w%.

To put these results into perspective, they can be compared with similar ballast blocks soaked in NaOH 1.0w% with and without electrolysis (Figure 4a). These treatments required on average 150 days to reach 90% of the total Cl^- released, and over one year for total stabilization.

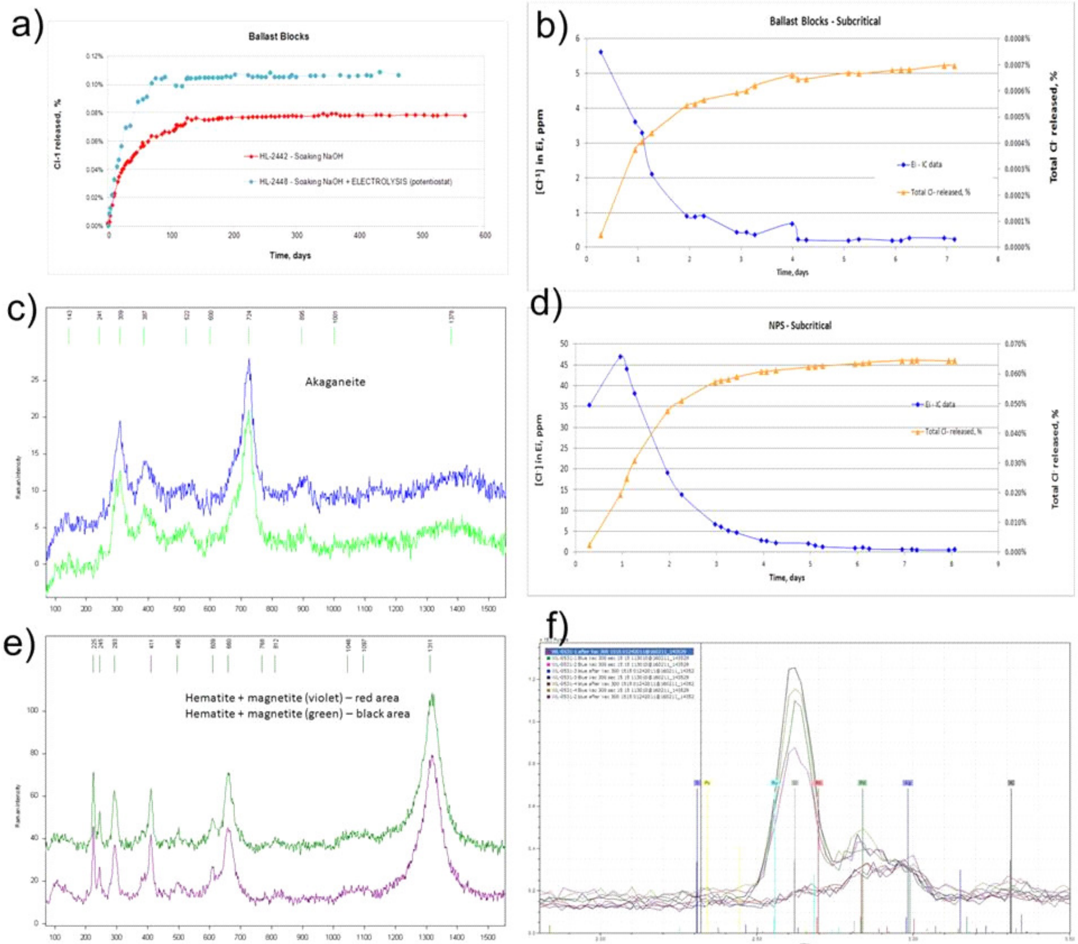

Figure 4: Analytical results: a. Cl^- release during conventional treatments of two ballast blocks; b. Cl^- release during subcritical mass-treatment of five ballast blocks; c. Pre-treatment micro-Raman spectrum identifying akagenéite on NPS artifact; d. Cl^- release during subcritical mass-treatment of nine NPS artifacts; e. Post-treatment micro-Raman spectrum of transformed corrosion products on NPS artifact; f. XRF spectra before and after subcritical treatment identifying removal of chloride on NPS artifact.

The low amount of total Cl^- released during mass treatment of the five blocks group was an expected outcome. Considering that these blocks had been soaking in NaOH 1.0w% for over four years, it was anticipated that most of the Cl^- had been removed. Simple soaking in NaOH can be very effective for Cl^- removal providing the artifacts were never allowed to dry out and akaganéite was not present.

Localized color change from orange to black was noted, corresponding generally to lepidocrocite and magnetite respectively. Although superficial deposits had persevered, a change in the physical state of these features was soon noted. Even in the wet state, some of these deposits would readily brush off demonstrating a loss in adherence. This phenomenon has been recognized in previous work, and it has been suggested that increased porosity is due to changes in crystal lattice structure of the corrosion product matrix, and possible leaching out of substitutional and interstitial elements, such as sodium, calcium, chlorine and phosphorous respectively (González-Pereyra, *et al.* 2010: 39-49). Instead of utilizing hammers and chisels, cleaning could be performed using mostly a scalpel. The original surface, easily identified, had a compact near-metallic sheen throughout, and appeared somewhat consolidated. Where the benefits of carrying out cleaning procedures after stabilization and in the dry state were particularly accentuated was at the discovery of tool marks and foundry stamps on the ballast blocks, as shown in Figure 2.

Where considered necessary, a consolidative treatment by immersion in Owatrol™ oil – an alkyd-based drying oil with an inbuilt corrosion inhibitor was employed.

NPS artifacts

With these artifacts, a slightly different approach was employed. As seen in the images, the artifacts had very little corrosion layers present to add to the overall volume of the artifact.

The challenge with already dry terrestrial artifacts with regards to stabilization treatments under immersion in varying solutions is the inherent physical stresses caused by not only the permeation of the solution into the crevices of the corroded artifact, but also the continued ionic exchange at the active corrosion sites. This is particularly accentuated at pit and blister sites, where the original surface is often forced away from the artifact causing separation and loss of surface detail. Thus chemical stabilization and desalination of dry and terrestrial iron artifacts has been viewed as a considerably difficult and an unresolved issue in conservation (Drews, *et al.* 2004:247-260; Mardikian, *et al.* 2006:113-118; North, *et al.* 1978:174-186; Selwyn, *et al.* 1999:217-232; Watkinson 2010:3307-3340). To prevent any further stresses occurring within the artifacts during subcritical treatment the artifacts were soaked in the treatment solution for 72 hours prior to the run. It was completed in 8 days and the results can be seen in Figure 4d. The plot displays a typical behavior showing a Cl^- peak within the first day followed by a significant drop. Similarly to what was observed in the case of the first ballast block, approximately 95% of the total Cl^- released took place during the first four days. Post-treatment, SEM-EDS elemental analysis showed a level of chloride under the instrument detection limit of 0.1w%, while pre- and post treatment XRF analysis (Figure 4f) clearly illustrates elimination of chloride from the artifacts. Finally, SEM-EDS confirmed that subcritical conditions did not affect elements such as lead or copper.

The corrosion products of all the NPS artifacts were analyzed using micro-Raman spectroscopy in different areas of the artifact's surface. Analyzed areas were selected for their diversity in color and texture. Active corrosion was evident, occurring below the original surface, largely in pits with bright orange powdery corrosion products identified as akagenéite (Figure 4c). Lepidocrocite and goethite were found only in a few areas. A striking absence of akaganéite was observed after subcritical treatment, as illustrated in Figure 4e. The akagenéite had been converted to hematite with magnetite and goethite in localized areas.

From visual inspection and weight measurements, it was clear that no significant material loss had occurred during treatment, the oil-based consolidant and the number labels applied in a previous conservation campaign had effectively been removed. After analysis and in order to improve the general appearance of the artifacts, micro-air-abrasion was performed on the selected four artifacts. Although consolidation was not considered necessary with regards to the physical integrity of the artifacts, due to an agreement with the NPS, they received a consolidant in the form of Owatrol™ in two applications, with the last application slightly pigmented with natural magnetite powder. This treatment was performed to purely improve the appearance of the artifacts and to allow for assessment of a contrast between a stabilized and a fully conserved artifact.

Conclusion

Recent experiments using subcritical fluids have shown great promise of resolving many of the issues relating to the stabilization of archaeological iron – marine and terrestrial. The results of this work have encouraged further research and experimentation to improve the methodology and its applicability across the field. Recent focus on such development has revolved around the possibility of modifying the reactor capabilities in order to be able to carry out rinsing and drying within the treatment chamber. Further yet, considerations have been made towards an unfathomable advancement, where subcritical and supercritical technologies would be combined to allow for the inclusion of the application of tailored corrosion inhibitors and consolidants during a single step in the treatment. In addition small-scale laboratory testing has been initiated to study the effect this fluid technology may have on non-ferrous metals. In short, extensive continued research is necessary in order to implement an integral treatment for metallic cultural heritage, that is effective, fast, reversible, sustainable, safe, and in accordance with conservation ethics.

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