



Potential Applications of Supercritical Carbon Dioxide
Extraction and Impregnation for the Stabilization and
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and Impregnation for the Stabilization and Conservation
of Industrial Heritage Artifacts**

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**Novel Techniques for Stabilization and Conservation of
Ferrous Metals in Industrial Heritage**

Michigan Technological University Proposal #1110065

Timothy James Scarlett, Principal Investigator

Project Team:

Gerard Caneba, Co-PI

Alexander Atkinson

Eric Pomber

Stephanie Tankersly

Shubham Barole

Katherine Trotter

Alexander Whydell

Steven Moray

Brendan Peltó

Alejandra Alvarez

Mark Dice

With contributions by or support from:

Gerald Anzalone

Owen Mills

Edward Laitila

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1. Executive Summary (400 words)

An interdisciplinary team of students from Michigan Technological University completed a series of tests using Supercritical Carbon Dioxide (SC-CO₂) to extract water and volatile compounds from samples of corroded archaeological iron artifacts. Test samples were then cracked and examined using backscatter SEM. Qualitative visual inspection showed that pores and microfissures were clear and opened after SC-CO₂ extraction. Another SC-CO₂ treatment then impregnated the test objects with an environmentally-benign polymer (Acryloid/Paraloid™ B-72) to consolidate fragile structures and seal objects against future water absorption. Following treatment, these samples were also cracked and examined with SEM. Chemical traces of the polymer demonstrated the complete diffusion of the B72 into the pores and microfissures of the sample. These tests were paralleled by the design and execution of traditional conservation plans for twenty ferrous metal artifacts. The project team developed essential comparative perspectives on existing techniques, while being engaged in considerations of professional ethics, practicality, and economic value.

This study showed that the emerging application of Supercritical Fluid (SCF) Extraction can be used to rapidly stabilize batches of corroded ferrous metal artifacts, including cast and wrought iron and steel, as well as composite artifacts. This will allow labs to avoid or safely delay traditional electrochemical techniques that can require months of expert treatment. This technique works as a batch operation, allowing groups of small artifacts to be quickly stabilized and consolidated, potentially even in field settings. The process may also be tailored to treat objects from sites with soil contamination or materials from heritage collections, where potentially hazardous chemicals are also extracted during dewatering. While critically important questions remain to be addressed before the technique can be made systematically operational, particularly those surrounding chloride salts, the technique has tremendous potential to improve best practices in metals conservation. Our proof-of-concept experiments allowed us to improve our procedures for the next phase of development.

Students and faculty disseminated their findings at four separate archaeological and conservation conferences where results could be disseminated to different professional communities. Team members also prepared blog posts about their experiments targeted to public audiences. The project established a sustained collaborative relationship between the Departments of Social Sciences, Materials Science and Engineering, and Chemical Engineering at Michigan Technological University. Project scientists also developed professional connections with practicing conservators for future collaborations.

2. Introduction

Between 2013 and 2015, Michigan Technological University assembled a small interdisciplinary team of undergraduate and graduate students to undertake a proof-of-concept study in novel conservation techniques while building collaborative capacity among units. Working on research supported by the National Park Service's National Center for Preservation Technology and Training, the students undertook experiments applying Supercritical Carbon Dioxide (SC-CO₂) treatment to novel applications of dewatering, stabilizing/consolidating, and sealing corroded ferrous metal artifacts from archaeological sites. Supervised by Timothy James Scarlett and Gerard Caneba, the student team undertook experiments with sacrificial iron artifacts while also learning traditional conservation techniques. Their work revealed that SC-CO₂ treatments hold excellent promise for new treatment practices that are ethical, highly functional, and notably cost effective.

Historic preservation professionals need improved techniques for managing iron and steel artifacts from archaeological sites, museums, buildings, monuments and other heritage resources. These experiments represented a new collaboration for the researchers at Michigan Tech, but the University is a compelling place to help meet this national need. While there are no conservation professionals on the faculty, the Department of Social Sciences focus on Industrial Heritage and Industrial Archaeology (IA or IH&A) provided a unique starting point for research and training. The university's considerable expertise in chemical engineering, including the resources of the Center for Environmentally-Benign Functional Materials (CEBFM), provided guidance on polymerization and supercritical chemistry. This collaboration established a working relationship between these faculty, created opportunities for archaeology, history, materials science, and chemical engineering students to earn technical training in conservation, exposed students in engineering to applied problems of heritage preservation, and connected the University's faculty with professional conservators working with industrial heritage. This collaborative work is leading to new proposals seeking funds to support a post-doc position in conservation science at Michigan Technological University and established the university as a qualified conservation laboratory in a region of the United States where the nearest similar facility is 600 to 1,000 miles away.

2.1 National Need

Industrial Heritage includes "traditionally-scaled" archaeological sites and artifacts concerned with the recent past, but also includes engineering landmarks, historic and architectural monuments, and collections of material often nicknamed "Big Stuff." There are growing numbers of industrial heritage museums and sites in the United States, many operated by local historical societies, but increasingly also operated by state and federal agencies, including more than a dozen National Historical Parks and National Heritage Areas. This is a growing international movement with roots in Industrial Archaeology. At the international level, UNESCO and ICOMOS collaborate with The International Committee for the Preservation of

the Industrial Heritage (TICCIH) to include sites in the World Heritage List. Of the 702 Cultural World Heritage sites, more than 5% are exemplars of industrial heritage like coal and iron mines; steel and textile mills; transportation networks; and the communities that supported them.

These heritage sites present complex stabilization and preservation problems, particularly those associated with iron, steel, and ferrous metal materials. The objects range from hand tools and machine parts, the traditional scale for museum conservation professionals, to purpose-built structures like blast furnaces, architecture, and infrastructure (i.e. monuments). Unlike the archaeology of households, excavations at workplaces in the industrial era often produce very large assemblages of corroded ferrous metal artifacts that overwhelm repositories. Traditional conservation strategies for ferrous metals (desalinization, electrolytic reduction, chemical or thermal dewatering, and sealing) are often unsatisfactory, overly intrusive, slow and expensive, or impractical (Rodgers 2004; Newman 2002; Watson, Fell, and Jones 2008). New materials and processes, particularly silicone-based polymers for objects (Smith 2003) and anti-corrosive paints and transparent coatings for technical monuments and architecture have been offered as potential improvements (Shashoua, Taube and Holst 2009; Conrads 2008; Mottner et al. 2008; and older work by Seipelt, Pilz; and Kiesenberg 1998; Brüggerhoff et al. 2008; Kiesenberg 1997; Seipelt and Brüggerhoff 1997).

Professional interests in industrial heritage have expanded with the basic economic drivers of this type of heritage: urban revitalization, post-industrial adaptive reuse of structures, brownfields remediation and superfund programs, etc. Big boosts to “Technical objects” conservation and “Industrial monument conservation,” spread through efforts like the EU’s creation of the European Route of Industrial Heritage, which connected museums and heritage sites through the network. This has spread to North America as the international interest has coalesced around the “Big Stuff” conference. This occurred concurrent with the rise of the “curation crisis” in SHPO approved collections management facilities around the United States. The United States federal government alone curates more than 60 million archaeological artifacts, figures that do not include antiques or objects held by state, local, and not-for-profit institutions in the country.¹ Any treatment that can save time and money bringing collections into statutory compliance will provide tremendous financial benefit to the system.

Museums and collections facilities clearly need conservators trained to work with industrial heritage and they need more options for conservation treatments. As indicated above, many industrial heritage museums lack extensive professional staff or facilities, so staff require low-cost conservation treatments appropriate for their geographic and economic situations. In addition, the use wear, gouges, grease, and corrosion on artifacts are often important to telling the story of mine work, for example, which leads professionals to debate traditional cleaning and painting of metal artifacts and surfaces. Given these issues, supercritical and subcritical fluid

¹ No reliable estimates exist about this situation. Some information can be found here: http://www.nps.gov/archeology/collections/repos_pr.htm.

treatments will undoubtedly play an important role in future preservation of the industrial heritage.

2.2. Iron and Ferrous Metals Corrosion

“Rust Never Sleeps” is a slogan of the Rust-Oleum Corporation and became a useful catch-phrase for a Parks Canada Publication (Ankersmit et al. 2008) intended to help non-professional and volunteer staff at museums and heritage sites understand the corrosion of iron and ferrous metal objects. This report is not the appropriate place for a full discussion of the origins of iron technology and the character of ferrous compounds, but the forms of iron and steel that humans find useful in our lives are fundamentally unstable. In ambient environmental conditions, iron and steel will begin to decay through electrochemical reaction with water, oxygen, and salts. Ferrous metal artifacts recovered from archaeological sites, as a consequence, are always decayed. Slowing or halting that decay is a thorny problem for conservation professionals. Donny L. Hamilton (1997) provided detailed discussions of metals corrosion, which is briefly summarized below (see also Watkinson and Lewis 2005; Navrotsky, Mazeina, and Majzlan 2008). Various traditional conservation treatments can also be found in North (1987), Rodgers (1992, 2004), Cronyn (1990).

Oxidation is the most common form of iron corrosion, an electrochemical process during which iron atoms lose electrons and become positive ions. Electron flow is essential for oxidation, as iron ions will then bond with oxygen, hydroxyls, or other molecules to enter a more stable ambient state. Iron is highly reactive because of its electromotive force (EMF) and it decays into a large number of corrosion products depending upon its post-manufacture structure and the environmental and contextual conditions. Anything that facilitates the movement of electrons in the environment, such as salts in solution, will facilitate decay. Decay can also be bioelectrochemical, such as when microorganisms in anaerobic or anoxic settings rich in sulfates (like seawater) react with iron to form Iron Sulfide. Iron oxide decay products include a “bewildering array” of polymorphs, including at least 20 major types discussed in the literature (Cook and Peterson 2005; González et al 2004; Majzlan 2008, 1635; Matthiesen, Hilbert, and Gregory 2003; Navrotsky, Mazeina, and Neff 2012; Refait and Glenin 1997; Réguer et al 2015):

Anhydrous Ferric Oxides:

Common:

Alpha-phase hematite ($\alpha\text{-Fe}_2\text{O}_3$) “Brown Rust” most stable at ambient conditions

Gamma-phase maghemite ($\gamma\text{-Fe}_2\text{O}_3$)

Iron (II,III) Oxide a.k.a. magnetite “Black Rust” (Fe_3O_4)

Hydrated Iron Oxide a.k.a. “Red Rust” ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$)



Figure 1. A wrought iron machine bolt from the West Point Foundry site curated at Michigan Technological University. The corrosion visible here is typical of decay of ferrous metals from that site. Active decay at the interface between the corrosion patina layer and the remaining iron core destabilizes the adhesion of the corrosion product to the iron core. Delamination such as this results when RH is above about 20%. Photo: Timothy Scarlett

Less common:

Epsilon-phase iron oxide ($\epsilon\text{-Fe}_2\text{O}_3$)

Beta-phase magnetite ($\beta\text{-Fe}_2\text{O}_3\cdot\text{Fe}_3\text{O}_4$)

Iron (II) Oxide (FeO), Wüstite (Fe_{1-x}O)

Siderite (FeCO_3)

Chukanovite ($\text{Fe}_2(\text{OH})_2\text{CO}_3$)

Iron Oxyhydroxides, Hydrated Iron (III) Oxide (FeOOH)

Goethite ($\alpha\text{-FeOOH}$) most stable at ambient conditions

Lepidocrocite ($\gamma\text{-FeOOH}$)

Akaganéite ($\beta\text{-FeOOH}$)

Hydrated forms, "Yellow Rust" ($\text{FeOOH}\cdot\text{H}_2\text{O}$)

Iron Hydroxides

Ferrous Hydroxide ($\text{Fe}(\text{OH})_2$)

Ferrihydrite ($\text{Fe}(\text{OH})_3$)

Other polymorphs

Cl- and S- products:

Ferrous chloride (FeCl_2)

Ferrous chloride dihydrate ($\text{FeCl}_2\cdot 2\text{H}_2\text{O}$)

Ferrous chloride tetrahydrate ($\text{FeCl}_2\cdot 4\text{H}_2\text{O}$)

Ferrous Hydroxychloride $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$ sometimes called Ferrous Hydroxysalt.

Ferric chloride (FeCl_3)

Rozenite ($\text{Fe}(\text{SO}_4)\cdot 4\text{H}_2\text{O}$)

Greigite (Fe_3S_4)

Ammoniojarosite ($\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$) and other jarosite compounds.

"Green Rust" a mixed-valence ferrous (Fe^{+2}) and ferric (Fe^{+3}) hydroxide and oxyhydroxide of variable Cl⁻¹ content. (North (1982:81) provides an example that ranges from "4Fe(OH)•FeOCl to 2.17 Fe(OH)2•1.83 FeO(OH)•FeOCl with a chloride content of 7.5% to 8% by weight.")

Conservators are concerned by these different oxides of iron because they all have different structures and various reactivity and stability. Hematite and Goethite are mostly stable at ambient conditions, where the corrosion layer forms a protective patina on an object. Akaganéite and Ferric Chloride will continue to react with the remaining iron core at the interface with the corrosion layer, converting it into new oxide or hydroxide compounds, unless interrupted through a conservation intervention (Selwyn, Sirois, and Argyropoulos 1999; Cook and Peterson 2005).

From the perspective of both the archaeologist's and conservator's professional ethics, decay should ideally be preserved as part of the artifact. Decay is a "natural" part of the life cycle of ferrous metal artifacts. As such, the corrosion product can be part of the use-life of an artifact or may fossilize surface or structural details. Ongoing and active corrosion becomes a problem because the new electron bonds lead to the formation of different molecular structures, which cause consequent changes in shapes of molecules and crystal forms. These changes deform objects by causing swelling, delamination, blistering, flaking, and other

changes in shape/volume; changes in compressive and tensile strength of the material; shifts in color, texture and appearance; and so on.

The ethical practice of both conservators and archaeologists call for a minimal intervention strategy (Hamilton 1999, 6-7). Preferred methods involve stabilizing, consolidating, and preserving artifacts, and therefore minimal cleaning is preferred and irreversible chemical, material, or structural alterations to objects should be avoided. This “do no harm” perspective must be compromised for other needs, including destructive investigative analyses, preparation and restoration for exhibition, financial practicalities, conflicting social values, or legal mandates.

2.3. Traditional Conservation Practices

Best practices for the conservation of ferrous metal objects have been changing, as conservators shift away from more intrusive practices. Because iron decays so quickly and the effects of that corrosion can be so damaging, past practice of conservators has been to intervene. In a basic sense, these practices evolved before professionals had a clear understanding of the different kinds of corrosion products and the different processes that govern their formation (Rodgers 2004 71-104).

As mentioned above, the key to most corrosion is the presence of liquid or vapor water, which facilitates the movement of electrons, provides oxygen and hydroxyl atoms, and easily dissolves salts into electrolytic solutions. When corroded iron seems dry to the touch, liquid water often remains sealed underneath the corrosion layers, trapped in pores and fissures, weakly bonded to molecules, and even adhered as a thin film the object’s surfaces. Conservators have therefore felt the need to remove the corrosion layer from the object, because doing so allows them to extract the water trapped at the interface, extract salts or other ions from that surface, and create and stabilize a new patina surface. Historically, conservators have accomplished these tasks with various methods:

- Removal of corrosion via mechanical mechanism (abrasion, microbead abrasion, laser ablation, hydrogen plasma oxidation, etc.) or chemical mechanism (electrolysis, galvanic, etc.)

- Removal of salts by soaking in distilled water or chemical bath.

- Creation of patina using tannic acid or related products.

- Sealing objects to protect new patina using wax, polyurethane, or other products.

While conservators have generally followed the projections of “do no harm” and minimalist intervention (Rodgers 2004, 12-16), their need to be thorough and cost effective when removing the corrosion layer pushed professionals to use electrolytic cleaning despite its irreversibility. Since most small institutions do not have access to laser, plasma, or microbead abrasion cleaning systems, electrolysis is common as it requires only simple equipment and basic training. The results of this intervention have become less popular in current professional practice, however, because the treatment destroys the surface character of material by altering its color and texture, plating an artifact with new metal while exacerbating pitting on cast iron and delaminating wrought iron. Tannic or other acid treatments also dramatically darken objects and obscure surface details, which is further exacerbated by coats of polyurethane, wax, or other sealants. Conservators are now

moving away from these treatments (Wang 2007). Finally, doing electrolytic cleaning well requires a great deal of time and expertise, particularly for large objects commonly held by industrial heritage museums and facilities. Professional conservators have shifted to a lighter touch stressing mechanical cleaning over chemical or electrochemical (Newman 2002, 44-46), often focusing on how corrosion can be controlled by careful management of the conditions in which objects are stored, particularly humidity and temperature. Those working with objects from maritime sites however, such as shipwrecks and inundated landscapes, generally still use electrolytic processing because of problems specific to salt water contamination (Watkinson 2010, 3320-3321; Rodgers 2004, 71-104).

2.4. The Challenge of Salts

This study was not designed to examine the problem of chloride and salts in artifact conservation. In recent years, the terrestrial industrial sites studied by Michigan Technological University's archaeologists have been part of temperate freshwater environments with little contamination. While iron artifacts are conserved in our lab, team members use Chloride Test Strips for repeated testing of the deionized water and electrolytic bath solutions in which artifacts soak. Artifacts from sites like the Cliff Mine have not yet exhibited detectible levels of chloride contamination.

That said, the problem of salts must be reviewed here because chloride contamination and its role in corrosion is critical to the conservation processes discussed in this report. Supercritical and subcritical fluid treatments may now finally help resolve challenges of chloride "washing" in a rapid batch processes (see Section 4.c below). Conservators have long recognized the expense and time demands of extracting chlorides, for example, experimenting with batch-style heat treatments (North and Pearson 1977). But while batch treatments like heat treating can be shown to eliminate chloride contamination, they also altered the metallurgical structure of artifacts and thus were considered unacceptable solutions to the problem.

Chlorides are destructive to iron and their removal when present must be a part of any conservation plan. These ions facilitate ongoing decay when they are trapped at the interface between corrosion nodules and the remaining iron body and they can also become incorporated into mineralizations (Wang 2007). Once mineralized into akaganéite, for example, the chlorides become insoluble in water and are nearly impossible to remove without highly caustic chemical treatments (Cook and Peterson 2005; de Viviés et al 2007). Akaganéite (β -FeO(OH)) is a "chloride-hosting iron oxyhydroxide", and the chlorides held by it are among the most difficult to remove without radical intervention (Näsänen, González-Pereyra, and Cretté 2011).

The removal of chlorides is currently a slow process where artifacts are soaked in a bath of deionized water. During this bath, which may last weeks, months, or even years for large objects, the chlorides continually diffuse into the water through osmosis. While this soaking bath could be a batch process for groups of artifacts, such treatment prevents direct attribution of chloride levels in solution to individual objects. The diffusion is chaotic but has been modeled (Selwyn, McKinnon, and Argyropoulos 2001) and can be generally characterized as a two-

stage process, relatively rapid at first and then much more slowly in the second stage process (Weizhen and Chunchun 2005), unless the bath is refreshed regularly. This process can be accelerated by the use of lithium hydroxide, sodium sulphite, sodium hydroxide, sodium carbonate, or aqueous 1,2-diaminoethane (ethylenediamine, EN) solutions instead of pure deionized water, but all these are caustic solutions. Some of these chemicals present health and safety risks for lab staff and are burdensome for waste disposal (González et al 2004, Näsänen, González-Pereyra, and Cretté 2011, Selwyn and Argyropoulos 2005). Higher rates of desalination can also be achieved through the application of pulsating current in an electrolyte bath (Dalard, Gourbeyre, and Degriigny 2002; Liu, Li, and Wu 2008).

In trying to mitigate for chlorides and other corrosion processes, conservation scientists have tried other methods to slow reactions. They have made great progress identifying different corrosion products and modeling their evolution between various phases and into alternate compounds, over time and under various conditions (Neff 2012; Neff et al 2005; Navrotsky, Mazeina, and Majzlan 2008). With these new models, which often differentiate how materials chemisorb or physisorb atmospheric moisture to create new electrolyte, conservators know why different corrosion products are stable or become active in certain conditions. No matter what treatments are used to stabilize iron artifacts, for example, they should later be stored at or below 12% relative humidity (RH). At 15% RH, akaganéite begins corroding iron, with increasing RH producing a faster corrosion rate. Above 20% RH, ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) starts to form and add to the overall corrosion rate. At 25% and above RH, the rate of decay increases dramatically for all types of reactions (Watkinson and Lewis 2005). Many industrial heritage facilities that hold artifact collections do not have curatorial storage that meets professional standards and can not afford to build facilities with operational HVAC that can hold RH continually at such low levels. In many cases, decay will resume after conservation and sealing and iron must be monitored closely for ongoing decay (c.f. Pingitore 2015).

2.5. Supercritical and Subcritical Fluid Techniques

Professionals are pushing to develop new techniques of conservation for ferrous metals that can extract water; remove chlorides, salts, and other harmful ions; develop thin film coatings to seal surfaces against reabsorption without detracting from surface detail; are reversible; and which are fast, long lasting, and therefore cost effective. Supercritical and Subcritical Fluid techniques are perhaps the most promising of all those in development. While the technique entered professional practice more than twenty years ago (Kaye and Cole-Hamilton 1994), high-pressure treatments have attracted more interest in the past decade.

Supercritical and subcritical fluid extractions (SFE) are widely used in industrial processes, including decaffeinating coffee beans. J. Memet (2008) explained that conservators first became aware of supercritical and subcritical fluid treatments from French industrial applications for cleaning sheet metals and manufacturing pharmaceuticals. While the industries started applying SC- CO_2 extraction in the 1970s to decaffeinate coffee beans, the technique is now very widely used to extract, separate, and purify natural and synthetic chemicals; clean clothing

and precision machinery; synthesize and process polymers; and apply a wide variety of coatings (Cretté et al 2012, 3). Most recently, Rowe et al. (2013) applied SC-CO₂ extraction as a non-destructive method for removing contaminating organic residues from mummified human remains prepared for AMS dating, replacing harsh acid treatments. These techniques involve using a fluid as a solvent, but by controlling temperature and pressure so that the fluid enters a sub- or supercritical phase and, in the latter, the fluid is no longer a liquid or a gas (Figure 2). In this phase, fluids exhibit properties of high diffusivity, low density, low viscosity, and low surface tension. Matter in a supercritical phase² can effuse into another solid as a gas while at the same time acting as a liquid solvent. The lack of surface tension means no behavior to interrupt effusing movement. Using a supercritical fluid like carbon dioxide as a solvent then allows the fluid to effuse through a solid where it can dissolve volatile (and some nonvolatile) liquids from exterior *and interior* surfaces of porous materials. As pressure is released, the CO₂ enters into a gas phase and the extracted compounds are evacuated from the pressure chamber along with the gas.

Supercritical fluid extraction is a powerful tool in industry, where technicians can generally “tune” the process to control which element(s) are extracted from a complex sample. Laboratories will control temperature, pressure, flow rate, and processing time in order to adjust the extraction process. Carbon Dioxide is the most common supercritical fluid used in industry, followed by water as another popular choice. The supercritical process allows industrial applications to replace caustic solvent solutions with more benign fluids used at high pressure.

Supercritical Fluid Extraction (SFE) has been used with carbon dioxide fluid (SC-CO₂) by small groups in conservation science. We initially designed our experiments based upon the study by Eric Schindelholz (2007), undertaken when he was at the National Park Service’s Harpers Ferry Center. That study was based upon the pioneering work by a team at the University of St. Andrews (Kaye and Cole-Hamilton 1994, 1998; Kaye, Cole-Hamilton and Morphet, 2000). Since beginning our proof-of-concept study, we also found the publications by the conservation group at Clemson University’s Warren Lasch Conservation Center who have applied *subcritical* processes in work on the submarine CSS H.L. Hunley (see cited publications by Näsänen, González-Pereyra, Cretté, Mardikian, Drews, Bayle and others). They are now collaborating with the French conservation firm A-Corros (de Viviés 2007, Memet 2008, and Neff 2012). A team working on the USS Monitor has also run SC-CO₂ experiments (Cook and Peterson 2005).

² All matter can move between various phases, the fundamental phases are gas, liquid, solid, and plasma. A material moves between different phases as conditions of temperature and pressure change. So while water shifts from a liquid to a solid at 32°F/0°C, when at 1 atmosphere of pressure, if pressure were to increase, water will remain in the liquid phase at that temperature. Carbon dioxide is a solid at -109.3°F or -78.5°C while at 1 atmosphere, a phase commonly known as dry ice (Figures 2 and 3). The CO₂ will begin to sublime into gas as it warms up, unless the pressure is increased proportionally to force it into the liquid phase (or even back into the solid phase).

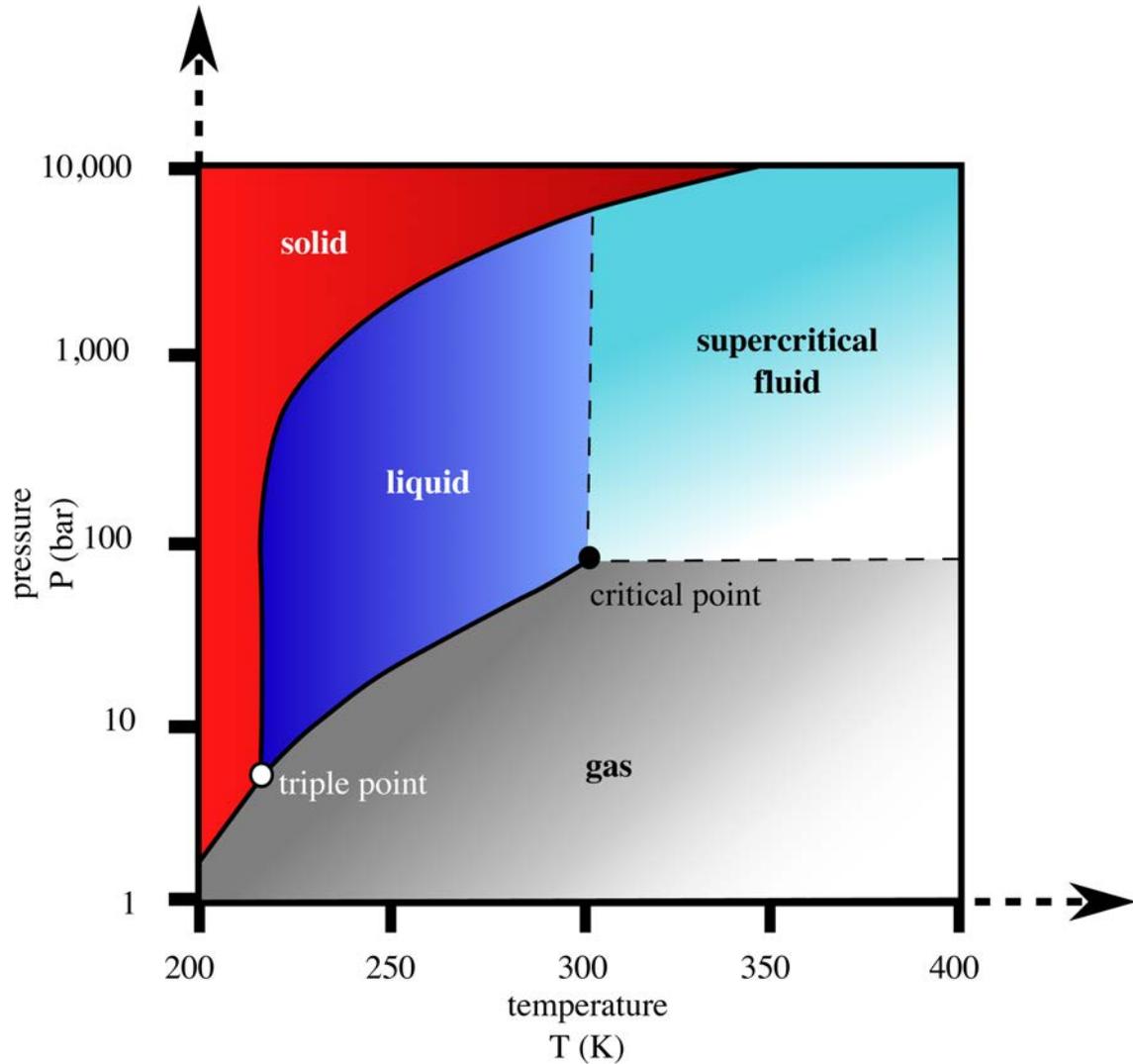


Figure 2. Pressure-Temperature Phase Diagram showing the point at which carbon dioxide can simultaneously exist as a liquid, gas, and solid (the “Triple Point”) and the area where it enters supercritical phase, above critical temperature of 31°C ($\approx 88^{\circ}\text{F}$, $\approx 300^{\circ}\text{K}$) and critical pressure of 73 atmospheres (≈ 74 bars). "Carbon dioxide pressure-temperature phase diagram" by Ben Finney and Mark Jacobs. Licensed under CC0 via Commons - https://commons.wikimedia.org/wiki/File:Carbon_dioxide_pressure-temperature_phase_diagram.svg#/media/File:Carbon_dioxide_pressure-temperature_phase_diagram.svg

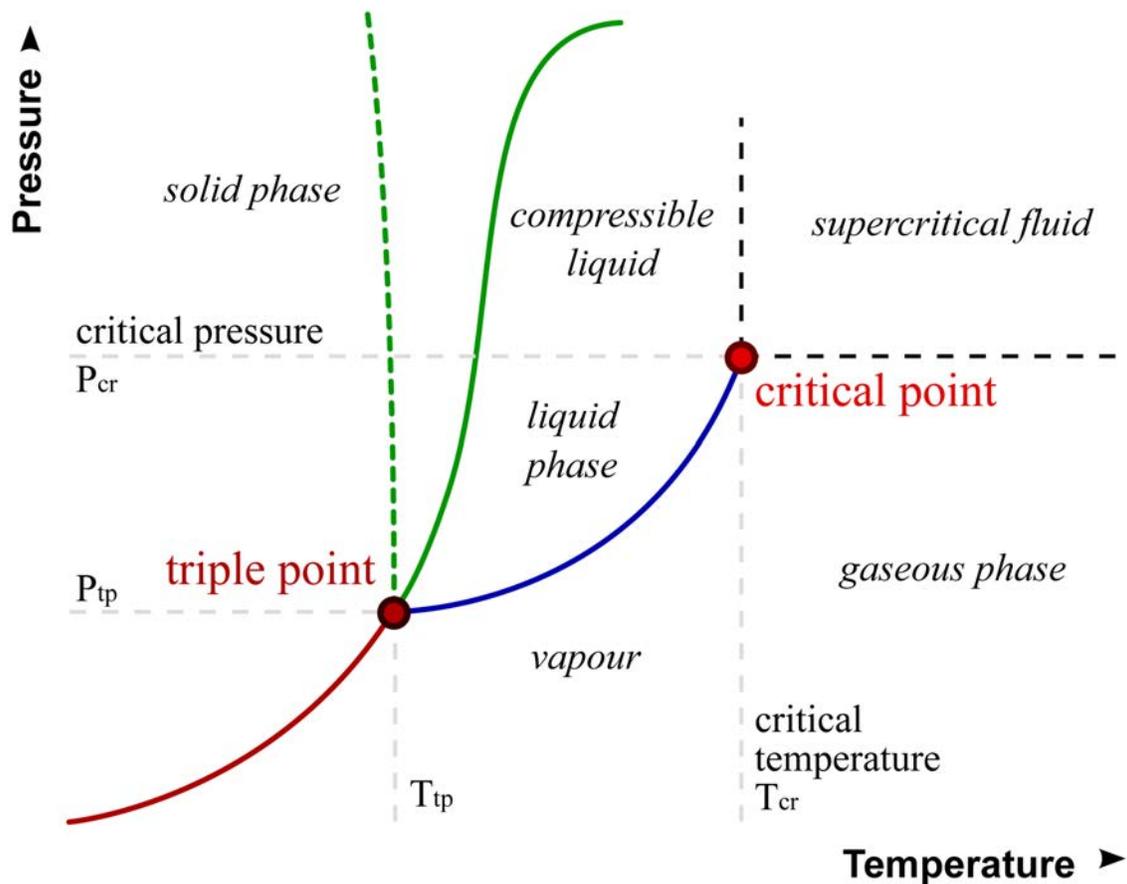


Figure 3. A generalized pressure-temperature phase diagram, illustrating the relationship between triple and critical points, how the freezing point can vary with pressure (represented by the solid green line), how the boiling point can vary with pressure (represented by the blue line), and the sublimation/deposition boundary (represented by the red line). Some “non-compressible” liquids exhibit odd freezing behavior, such as water, indicated here by the dotted green line. "Phase-diag2" by Matthieumarechal. Licensed under CC BY-SA 3.0 via Commons - <https://commons.wikimedia.org/wiki/File:Phase-diag2.svg#/media/File:Phase-diag2.svg>

Most conservation experiments thus far have focused upon using SC-CO₂ to treat organic materials, particularly wood and cork. More recently teams have tried to apply super- and subcritical treatments to iron, primarily with the goal of chloride extraction from maritime remains (these will be discussed further in Section 4d below). This study examined the question of how SC-CO₂ could be used to establish a batch-treatment process to dewater, consolidate, and impregnate and coat corroded iron with polymer sealant.

3. Methods and/or materials

Drs. Scarlett and Caneba recruited a team of students, including undergraduates from Social Sciences and Materials Science and Engineering, along with a graduate student from Chemical Engineering. The team designed and ran a series of experiments to assess the appropriateness and effectiveness of SC-CO₂ conservation treatments for iron and measure the potential life span. Supervised by Drs. Scarlett and Caneba, the students were also assisted in instrument work by Gerald Anzalone, Owen Mills, and Edward Laitila in the Department of Materials Science and Engineering.

Shubham Barole assembled the SCF extraction system equipment, illustrated in Figure 3. The syringe pump pressurized CO₂ into the c. 350 cc stainless steel “bomb.” The bomb is about the size and shape of a 12oz soda can (on the left side of the illustration). The bomb was equipped with an inlet valve, a pressure gage, and a thermocouple to measure internal temperature. The bomb was also wrapped with electric heating strips and sat in a chiller that allowed for temperature regulation. The pump controller allowed for a programmed rate of pressurization and would then hold the maximum pressure until the extraction cycle was complete.

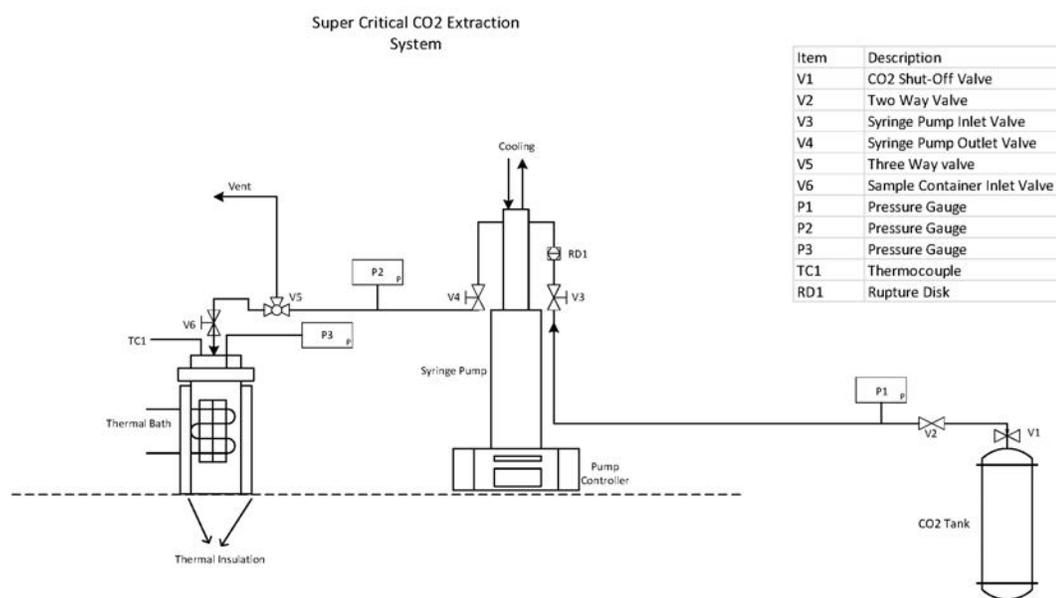


Figure 4. Diagram of the SCF extraction system equipment assembled in Michigan Technological University’s Center for Environmentally Benign Functional Materials lab. Credit: Shubham Barole/Michigan Tech.



Figure 5. Shubham Barole monitors the bomb pressure in the CEBFM. Photo: Eric Pomber.

During operation of all the trials, the CO₂ syringe pump filled overnight, building pressure. The syringe then injected the supercritical CO₂ fluid into the bomb within 1-5 minutes, rapidly raising the pressure in the chamber to 950-1000 Pound-Force per Square Inch (about 68 ATM or 69 Bar). The bomb was left at peak pressure for 12-24 hours to allow for effusion of CO₂ into samples and diffusion of water into CO₂ SCF. The bomb temperature started about 23°C and peaked and held at 60°C overnight. Researchers then released pressure in the bomb, starting slowly and then increasing the rate as pressure dropped in the bomb. The pressure dropped relatively rapidly, usually in about 1 minute. This decompression is very rapid compared to those used in comparative studies (Teshirogi et al. 2002). The rapid pace encouraged the quick evacuation of CO₂ as it shifted to gas phase, opening pore and fissure structures, and carrying dissolved moisture and other compounds out of the sample and into the released gas. The rationale for these procedures is discussed below.

Before initiating the formal study, the team ran a number of trials with the injector system in order to familiarize themselves with its operation and assess the effects of the process on corroded iron. It quickly became clear that the ferrous metal samples, no matter the state of their decay, were much more resistant to the shrinking or warping effects observed in wood subjected to the same treatments. In all cases, there were no noticeable changes to the samples after they had been run through SC-CO₂ extraction. The team therefore decided to drop their plans for digital scans of the test samples because the deformation analysis would not have been useful. Instead, the team shifted effort to extend their experiments into polymer selection and the long-term stability of polymer sealants.

The team intended the first set of samples to assess the ability of the system to extract water from the samples and open the pores and cracks. After those trials were complete and SEM imaging had been done, the team ran a series of experiments to see if SC-CO₂ could be used to effuse a polymer throughout the samples, as both a structural consolidant and a sealant to create a moisture barrier against rehydration and renewed corrosion processes. During these trials, the team experimented with different polymers, examining the effectiveness and surface appearance of two main treatments, Acryloid/Paraloid™ B-72 and Polyurethane. The team selected these polymers because conservators trust them for application to metals using traditional techniques, so using them would allow the team to focus on the application of SC-CO₂. Following those soaking tests and the assessment of the SC-CO₂ impregnations, however, the team designed simulations to get an idea of the expected lifespan of various polymer sealants that might be used in supercritical conservation.

Acryloid™ B-72 (also called Paraloid™, particularly in Europe) is ethyl methacrylate, a durable and non-yellowing acrylic co-polymer, commonly used in conservation sciences. At various concentrations, Acryloid™ is used as a consolidant for paintings (1%-5%), to stabilize wood (5%-20%), and as an adhesive (50%+) for many materials. B-72 is soluble in acetone, toluene and isopropanol. Many conservation laboratories prefer this polymer for a wide array of applications because it is resistant to discoloration (even at high temperatures), is very durable, is resistant to “water, alcohol, alkalis, acid, mineral oil, vegetable oils, and grease”

(Hamilton 2010, 12). It is also reversible because it remains soluble over long periods, probably 100 to 200 years, while also retaining considerable flexibility over time (Davidson and Brown 2012, 99-100).

Polyurethane (in this case by Minwax) is a thermoplastic polymer diluted in mineral spirits solvent (48%-50% wt.). Various polyurethane mixtures are used in iron conservation for sealing and protecting cleaned metals, generally when objects are too large to be immersed in and sealed by wax blends. Polyurethane is applied by brush and dries quickly into a clear, tough, and flexible coating. The dried coating is highly resistant to “moisture, salt water, acids, alkalis, abrasions, and weathering” (Hamilton 2010, 5-6). Coatings can be removed with aromatic and chlorinated solvents, such as toluene or ethylene dichloride, although complete removal can be difficult.

After soaking test samples in polyurethane and Acryloid/Paraloid™ B72, formulated at different weights, the team selected Acryloid/Paraloid™ at 10% weight solution in acetone for their tests. The team then chose artifacts for testing that would fit into the c. 350 cc bomb chamber. They also selected objects that they could then crack and examine in cross section, setting on a group of nails of varied manufacture and a small cast iron bar. The samples were run in batches during each cycle of the injector system, where they were placed together into a glass beaker and then set within the bomb chamber. After a particular treatment, researchers fractured the samples by immersing them in liquid nitrogen and then cutting them with a hammer and chisel upon an anvil. After cutting, one portion of the sample was retained for analysis and the other (larger) portion was returned for the next step in testing.

Eight samples (Table 1.a) were initially selected, including four cut nails and four wrought nails from the same depositional context. One of each nail type was retained as an untreated control sample (sample set “a”). Then six remaining samples were run through a SC-CO₂ extraction cycle to dewater the objects, and one of each nail type was retained after drying with no polymer treatment (sample set “b”). One of each nail type was returned to the bomb to be impregnated with B72 in the acetone solution during SC-CO₂ treatment (sample set “c”). The final two samples were soaked for 24 hours in the same polymer solution immediately after drying (sample set “d”). Examples from sets c and d were cracked, in the same manner described above, in order to examine the cross section.

Table 1: List of Samples, including only those from formal trials.

a. Main Test Sample List (Cliff Mine, Keweenaw County, Michigan):

Sample #	Material/Object	Treatment	Detail
ESS001a	Wrought Iron Nail	untreated	
ESS001b	Wrought Iron Nail	SC-CO ₂ dry only.	
ESS001c	Wrought Iron Nail	SC-CO ₂ dry, SC impreg.	10% wt. B72 in Acetone
ESS001d	Wrought Iron Nail	SC-CO ₂ dry, 24 hr. soak	10% wt. B72 in Acetone
ESS002a	Cut Iron Nail	Untreated	
ESS002b	Cut Iron Nail	SC-CO ₂ dry only	
ESS002c	Cut Iron Nail	SC-CO ₂ dry, SC impreg.	10% wt. B72 in Acetone
ESS002d	Cut Iron Nail	SC-CO ₂ dry, 24 hr. soak	10% wt. B72 in Acetone
ESS003	Wrt. Iron Spike	SC-CO ₂ dry, SC impreg.	10% wt. B72 in Acetone
ESS004	Cast Iron Rod	SC-CO ₂ dry, SC impreg.	10% wt. B72 in Acetone

All of the main test samples were from the Cliff Mine Archaeological Project collection (Stamp Mill Complex, Quad A, Level 2, Bag 23/174).

b. Archive Samples (West Point Foundry, Cold Spring, New York):

04-03-9B-9 Box 440	Wrought Iron Bolt, SC-CO ₂ dry, 24 hr. soak in 10% wt. B72 in Acetone.
04-04-04 F50	Wrought Iron Bolt w/ fused Washer. SC-CO ₂ dry, SC Impreg. Using 10% wt. B72 in Acetone, with Cut nail.



Figure 6. Samples ESS 003 and ESS 004, after chilling in liquid nitrogen, cracking (A), and placement in the bomb (B) prior to SCF treatment. Photos by Stephanie Tankersley.

3.1 SC-CO₂ Extraction

Samples were selected from surplus artifacts from the Cliff Mine site (20KE53), including wrought and cut nails and cast iron samples from the excavation of the 1850-1869 Stamp Mill Complex. The samples were chosen to establish a cross section of iron types and production processes, including nails made from iron rolled into plates and cut into shape and those that had been hand wrought, along with other objects that had been manufactured by casting. All samples had been cataloged following fieldwork and culled from permanent collection. The lab maintains a collection of these artifacts for use as expendable experimental samples.

The team ran initial trials with various small, corroded samples, most of which were intended to assess the effect of the SC-CO₂ treatment on the corroded iron structure so that they could design experiments and assessments of the technique's ability to dewater and then seal corroded artifacts. All SC-CO₂ extraction included several samples inside the bomb processed in small batches. Groups of samples were placed into a small glass beaker that was then sealed inside the bomb for treatment. This allowed the beaker to catch any loose flakes or nodules corrosion and hold liquid solutions.

The samples showed no signs of cracking, warping, delaminating, or any other changes in shape, regardless of the extent of corrosion, even with rapid decompression. The bomb chamber contained no loose grains or flakes of delaminated corrosion material. As a consequence of this, the team decided that the photogrammetric or 3D laser scanning done by Schindelholz (2007) was unnecessary. The iron samples, even when corroded into iron oxides, were robust enough that warping due to pressure changes would be negligible during this study.

3.1.1 Assessment of Extraction with ESM

In order to assess the microscopic effects of extraction, two samples (one SC-CO₂ treated and one untreated) were frozen with liquid nitrogen, then cracked to expose the cross section for SEM analysis. Mounted samples were examined with an FEI Philips XL 40 Environmental Scanning Microscope in a Low Vac Mode, equipped with an EDAX energy dispersive x-ray analyzer system (EDS). In this first study, the examination was only to make a qualitative assessment of any effects the SC-CO₂ extraction upon the iron samples at increasing depths below the surface.

When comparing SEM views of an untreated sample (ESS-002A) with a sample that was supercritically dried (ESS-002C, before impregnation), the supercritical treatment appears to have opened more pores and exhibited cleaner cracks than the untreated sample (Figure 7). From this we expect that SC-CO₂ extracted samples will have more surface area for the polymer to penetrate, embed, and adhere.

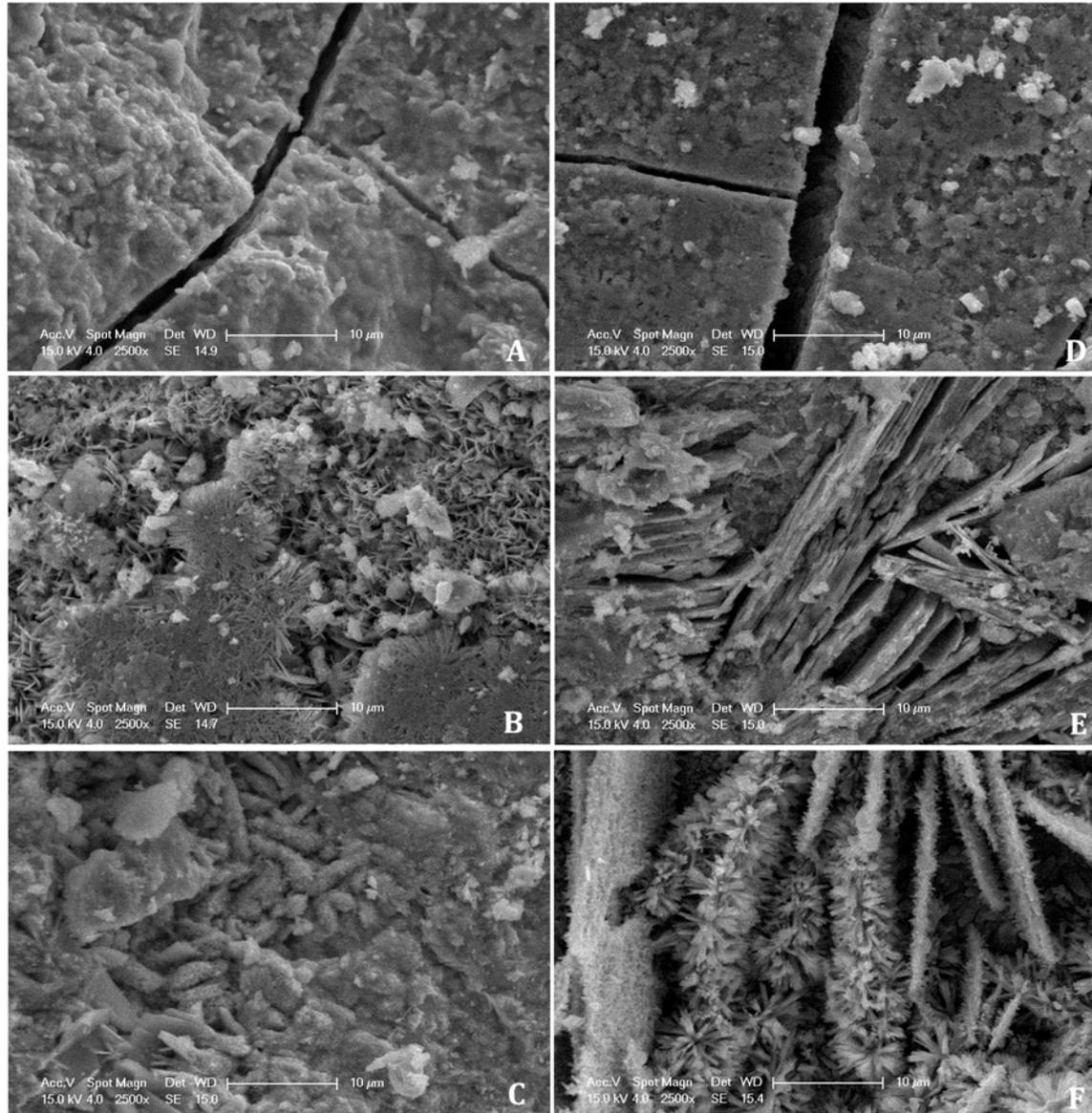


Figure 7. Six backscatter SEM images of two corroded iron nails in cross section, showing fissures, pores, and corrosion structures. A-C are from an untreated sample (ESS-002A). D-F are from a sample that was run through an SC-CO₂ extraction (ESS-002C). The qualitative analysis of these samples showed that the post-extraction sample exhibited “cleaner” and “more open” surfaces that indicate greater potential for diffusion or effusion by polymer for consolidation and sealing. Backscatter electron images were acquired using an FEI XL40 Environmental Scanning Electron Microscope (ESEM) equipped with an EDAX energy dispersive x-ray analyzer system (EDS). The ESEM was operating in low vacuum mode at a pressure of 0.3 Torr water vapor. Accelerating voltage was 15kV at a working distance of 10mm. Credit: Gerald Anzalone and Stephanie Tankersley, Michigan Technological University.

3.2. Polymer Impregnation

When it became clear that SC-CO₂ extraction removed water and other volatiles in samples, leaving the pores open, the team began to experiment with impregnations of polymers as sealants that would create an effective moisture barrier. The team reviewed polymers for the purpose, but as this was such a preliminary study, they opted for known and trusted conservation treatments, including Acryloid/Paraloid™ B-72 and Polyurethane.

The team conducted experiments in which they left some control samples untreated, the soaked samples in each polymer, and then they ran one set of samples through a SC-CO₂ cycle where the nails sat in solution within the bomb. The team did not seal untreated nails, since such treatment is well known to exacerbate corrosion.

3.2.1 Assessment: Scanning vs. SEM EBS Imaging

SEM Secondary Imaging could not specifically identify any polymer in the samples without adding some type of tracer dye to the acetone solution. The SEM Backscatter Imaging did reveal polymer, however, which is pictured in Figure 8. Brightest parts of images are most dense (iron), corrosion and slag are grey, and the polymer appears as very dark spots. The SEM confirmed these attributions by examining the elemental composition of the different materials. The metal was primarily iron, phosphorous and silicon. Slag had high silicon content, but less iron. The treated sample also has very dark spots that contain chlorine, potassium, calcium, and silicon (Acryloid/Paraloid™ B-72).

The penetration was complete, reaching several hundred microns into the sample. Precise measurement was not possible because the cracking method used to prepare the samples may have damaged them by shattering the polymer. In future studies, the team will adopt more efficient and quantitative techniques for measuring the polymer penetration into samples. Quantitative calculations could be possible if we add a tracer or dye to the polymer solution using two possible methods. In order to effectively use optical microscopy, a compatible fluorescent stain could be added to the polymer and a different fluorescent stain in the slide epoxy. One could then use epifluorescent illumination for optical microscopic void analysis and quantify the area of polymer filled pores and cracks vs. those that were filled by epoxy because they remained empty voids following SC-CO₂ treatment. This technique would have the added advantage of cutting and polishing samples stabilized in epoxy, which would reduce the shatter effect of the cracking technique used in this study. We could alternately continue to use SEM EBS if a unique tracer were added to the polymer, such as vapor stain like Ruthenium Tetroxide (RuO₄). That would allow measurement of that isotope over the cross section of the sample, including a continuous reading indicating the drop off of Ruthenium as the beam moved toward the center of the sample's cross section.

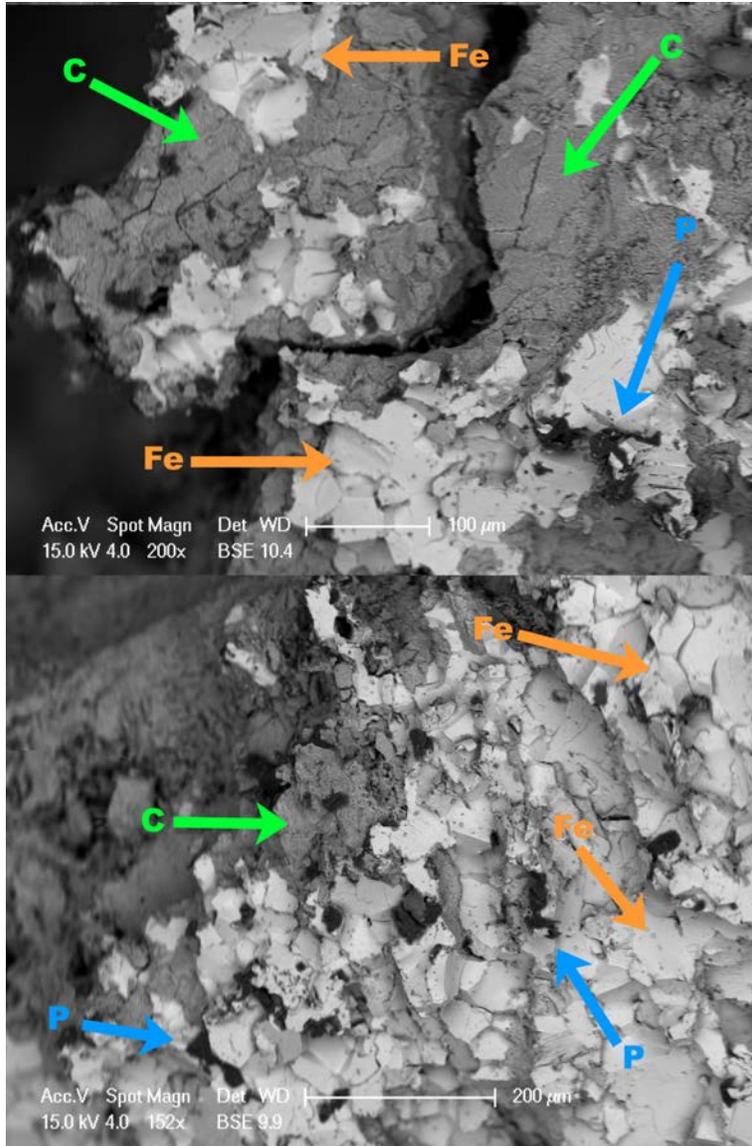


Figure 8. Two SEM backscatter Images of sample ESS002C, after SC-CO₂ Extraction and subsequent SC-CO₂ impregnation with Acryloid/Paraloid™ B-72 (10% solution in acetone). The brightest material in the backscatter images are iron (“Fe”, orange arrows), while corrosion and slag appear darker grey (“C”, green arrows). The polymer appears as very dark spots (“P”, blue arrows) that have compositions of chlorine, potassium, calcium and silicon. Polymer was observed filling voids deep into the sample, surpassing 300 microns in depth. Backscatter electron images were acquired using an FEI XL40 Environmental Scanning Electron Microscope (ESEM) equipped with an EDAX energy dispersive x-ray analyzer system (EDS). The ESEM was operating in low vacuum mode at a pressure of 0.3 Torr water vapor. Accelerating voltage was 15kV at a working distance of 10mm. These conditions permitted observation of the specimens without coating so as to maximize the chance of detecting polymer. These images of wrought iron samples were coated with platinum-palladium. Credit: Gerald Anzalone and Stephanie Tankersley, Michigan Technological University.

3.3 Assessment: Weathering

The treatment outcome left objects with a very thin film of Acryloid/Paraloid™ B72. This surface coat was thin and generally did not distract from aesthetic effect of the tested objects, considering texture, color, and finish. This coating could probably be thicker with no loss to these outcomes, so future experiments will have to add comparative trials with 20% and 30% solutions, or perhaps use a brush-applied top coat over an impregnated sample to assess changes. As the research team considered the conditions of storage and display of objects at local heritage sites and museums, they decided that some additional testing of the coatings was warranted. Industrial heritage's rusty objects are often displayed in small, community-owned or operated museums like local historical societies. As a result, iron objects are often stored and exhibited in the open, even outdoors. This raises concerns about how the polymer treatments would react or degrade when exposed to sunlight for long periods.

Because of concern for polymer weathering and degradation due to solar exposure, the team tested eight samples treated with Acryloid/Paraloid™ B72 and Polyurethane to see how they would age if objects with these treatments were stored in a manner that exposed them to direct or filtered sunlight. Among the eight steel washers prepared, two each were soaked in 10% Acryloid/Paraloid™ B72, 20% Acryloid/Paraloid™ B-72, 10% polyurethane. Once dry, the samples were then cured 4 hours with a Dymax BlueWave 200 UV Light Curing System. The coated washers were photographed at 2 hour and 4 hour marks during testing. Dymax staff estimated that UV exposure in New England on a sunny summer day could be around 3 mW/cm², or about 0.3 mW/cm² per hour of daylight. The BlueWave 200 provides about 20,000 mW/cm² per hour³. Each hour of exposure under the lamp is roughly equivalent to 6,667 days, or about 18 years of UV exposure. The polymers were photographed after 2 and 4 hours of exposure, simulating approximately 36 and 72 years respectively. While the polyurethane samples yellowed during testing, the Acryloid/Paraloid™ B72 showed no significant changes in color. The team exposed some samples treated with B72 for 24 hours without significant discoloration. From these tests, we concluded that UV exposure from open storage near windows will not appreciably degrade the visual effect of the Acryloid/Paraloid™ B72 coating.

Because many corroded ferrous metals have dark surfaces (“black” and “brown” rusts), any degradation of the polymers would not adversely effect the aesthetic appearance of treated artifacts. Those objects with brightly colored rust, “Yellow” and “Red” rusts, are generally hydrated rusts. The polymer coating darkens these surfaces slightly, but any sealer will have this effect. It is worth noting that the slight discoloring in these cases comes nowhere near the darkening effect of tannic acid treatments commonly used to create stable patina on ferrous metals. The SC-CO₂ process will dehydrate these structures, however, which will also change color in some situations. This is discussed further below, but more systematic tests are

³ Dymax staff do not recommend using the BlueWave 200 for weathering testing because this equipment is designed for use curing functional polymers.

necessary using these specific corrosion products in order to assess this potential problem.



Figure 9. Steel washers coated with Paraloid™ B72 (left) and Polyurethane (right) after 4 hours exposure with a Dymax BlueWave 200 UV Light Curing System. The Polyurethane shows significant discoloration compared with the Paraloid™.

3.4 Comparative Traditional Conservation Practices

Concurrent with the exploration of novel techniques to dehydrate, consolidate, and seal ferrous metal objects with SC-CO₂ treatment, student researchers also applied established conservation techniques to archaeological artifacts (Table 2). Team members conserved twenty different objects using a mixture of techniques ranging from soaking for chloride extraction, dehydrating through acetone bath, electrolytic removal of corrosion products, tannic acid treatment for patina, and sealing with B72 or archival wax blends. The general practice during these treatments was described in Deegan and Scarlett (2008) and is not repeated here in detail. These projects served to provide students with experience in technical practice that they could use when evaluating the effectiveness, usefulness, and ethical implications of their experimental outcomes with SC-CO₂.

Table 2. Traditional conservation plans executed during the project.

Object Description	Provenience Information	Collection
Horseshoe with intact nails	38S14W, Feature 27, Level 15, bag 153	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Brass shell casing	44S16W, Level 2, Bag 203	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Cuff Link	38S14W, Level 22, Bag 203	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Brass shell casing	38S14W, Level 19, Bag 175	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Small bronze pin or peg	38S14W, Feature 27, Level 9, Bag 125	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Cast iron shotgun shell crimper	38S14W, Feature 27, Level 20, Bag 191	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Cast iron bell-shaped object	39S12W, Level 1, Bag 208	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Cast iron latch assembly	28S14W, Level 18, Bag 173	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Hole-in-top iron can fragment	38S14W, Feature 27, Level 17, Bag 163	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Fragments iron can with lid	38S14W, Level 18, Bag 173-2	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Wrought iron cylinder and pin	38S18W, Feature 28, Level 2, Bag 137	Davenport Pottery site, Parowan, Utah, Utah Pottery Project Collection
Cast iron industrial jack	07172013-01	Lake Manganese Ravine, Keweenaw County, Michigan
Wrought iron hook	Quad D, Level 5, Bag 38.	Clifton Interyard, Cliff Mine Archaeological Project Collection.
Cast Iron stove fragment	Quad E, Level 6, Bag 206	Clifton Interyard, Cliff Mine Archaeological Project Collection.
Cast iron stove burner cover	Quad A, Level 6, Bag 37	Clifton Interyard, Cliff Mine Archaeological Project Collection.
Wrought iron composite chain	Bag 120	Clifton Interyard, Cliff Mine Archaeological Project Collection.
Iron hinge	Trench A, Level 1+S, Quad IV, Bag 4	Clifton Interyard, Cliff Mine Archaeological Project Collection.
Small iron padlock	Trench A, Level 2, Quad IV, Bag 83	Clifton Interyard, Cliff Mine Archaeological Project Collection.
Iron stamp mortar screen	SM 101.T12, Level 2.	Cliff Mine Stamp Mill, Cliff Mine Archaeological Project Collection.
Large cast iron stove door	50N19E-50N24E, Level 7.	Clifton Interyard, Cliff Mine Archaeological Project Collection.



Figure 10. These artifacts perfectly represent the potential of SC-CO₂ conservation for industrial heritage. This ladle and bolt were donated to Michigan Tech by someone who had collected them at a local smelter site. The objects are badly corroded. The bolt's surface details are entirely fossilized in the corrosion product. The wrought iron ladle, by contrast, contains no substantial iron core and is entirely corrosion product. It also likely contains hazardous compounds. SC-CO₂ extraction could remove the remaining water, effuse Paraloid™ B72 throughout the objects as a consolidant and barrier to water vapor, removing some toxics (such as mercury) and encapsulating other particulate matter (such as asbestos) currently encrusted within the corrosion product.

Table 2 summarizes the artifacts that were treated in these studies. The objects were from the Cliff Mine Archaeological Project and Utah Pottery Project collections curated in Michigan Technological University's Industrial Heritage and Archaeology facility. Treatments varied according to the nature and condition of each object, ranging from gentle cleaning with nylon bristle brushes (brass objects) to de-concretion with small steel chisels. Some artifacts were entirely composed of corrosion product with no intact metal core, such as parts of the padlock and the fragments of iron cans. The industrial jack, by contrast, was robust with only a thin surface of corrosion (although the internal surfaces of the formerly-moving parts could not be assessed). All objects were tested for chloride contamination using testing strips while soaking in a deionized water bath. Objects from Utah that tested

positive were soaked until the chlorides were no longer detected. Objects like the cast iron stove parts could all be effectively cleaned with electrolytic treatments. These treatments took from two to six months in the tanks, however, and not all artifacts responded favorably to electrolytic cleaning. The punched screen from the stamp mortar box was particularly resistant to cleaning in this manner. Following treatments, the objects were all returned to storage in the appropriate collection.

4. Results and Discussion

As discussed above, the tests demonstrate that supercritical carbon dioxide treatments are highly effective treatments for dewatering, consolidating, and sealing corroded iron artifacts. The procedure is safe, effective, and depending upon the choice of polymer, reversible. Labs could apply the procedure to batch loads of objects, including corroded masses of objects and some objects of composite materials. The objects could be treated as they are recovered and before or after using other conservation techniques. The procedure can be both effectively and ethically applied. While there remain a number of unanswered questions discussed below, we will seek additional resources to operationalize the technique.

As the samples remained in storage in ambient room conditions, repeated observations in the months following SC-CO₂ treatment revealed differences in the sample groups. None of these are surprising results:

1. As expected, untreated samples (group “a”) began delaminating in their bags within a few days or weeks. This process was rapid at first and continued at a slower rate over time. When corroded iron artifacts from terrestrial sites are allowed to dry, delamination is almost always observed. Once the artifacts dry out after removal from their moist soil context, ferrous compounds and amorphous materials undergo rapid aerial oxidation, changing into ferric oxyhydroxides (Selwyn, Sirois, and Argyropoulos 1999; Gilberg and Seeley 1982). These changes weaken the structural bonds between corrosion products and the iron core. The effect is similar to the manner in which the evolution of hydrogen can flake off corrosion during electrolytic treatment.
2. Those samples that were dried with SC-CO₂ extraction, but not sealed, quickly began rehydrating with atmospheric moisture while stored in polyethylene bags. After six months, this led to delaminating behavior similar to (but less severe than) the untreated samples.
3. Delamination was not observed on any SC-CO₂ dried and sealed samples at six months, which we interpret to mean that the objects were free of active decay. One of the samples soaked in the consolidant did begin exfoliating small grains of corrosion product between six months and one year. The archived wrought iron bolt sample (04-04-04-F50) had a bit of corrosion dust in its bag after one year. The cause of this was unclear. The sample bags were moved repeatedly during that time and mechanical stress may have caused small, impregnated pieces of corrosion to detach. It is also possible that vapor water may have filled irregularities in the surface of the polymer coating. This may be addressed in future experiments by using a 15%-20% B72 solution in acetone during treatment and by brushing objects with a

higher-concentration B72 coating upon the completion of SC-CO₂ treatment. This should impart a more robust surface to the consolidant.

4. The comparative conservation treatment plans produced good outcomes, but also unsurprisingly, generally took much, much longer. The cast iron stove door was cleaned using electrolytic processing and it spent many weeks in the first bath, then required retreatment again when chemical drying revealed that stubborn corrosion product remained in some cavities. This door was another ideal example of how SCF processes could aid conservation. If the door could have been lightly cleaned with electrolytic processes, but then a supercritical treatment used to extract all remaining water from the body, more corrosion could have been left intact on the object's surface (respecting the object's life history), preventing the pitting and somewhat uneven plating of the conserved surface, and providing for a complete moisture barrier seal throughout the areas of riveted repair (which are now weakened and at greater risk of developing new galvanic cells).

There is no indication of active corrosion on the SC-CO₂ impregnated artifacts, but this is difficult to measure on objects that have not been deconcreted or electrolytically cleaned. In the future, mass measurements may be required to genuinely test for the absence of decay over time in sealed artifacts. Watkinson (1983) demonstrated that volume:mass ratio can be an effective tool to measure an object's mineralization, which could be applied with these materials to track changes over a long period of time. No weeping has been observed on any artifacts, confirming expectation that no Iron(II) chloride or Iron(III) chloride (ferrous or ferric chlorides) are present. Further discussion of this monitoring problem continues below in 4.f.

SCF extraction and impregnation have tremendous promise as a basic batch treatment for archaeological and heritage collections, saving great deal of money in long term curation costs. The implications of our small study require additional discussion within the context of other existing literature, which lend greater significance to our findings. Facilities without adequate HVAC could use these treatments as a method to stabilize ferrous metal artifacts, and the literature points to composite artifacts and those of other materials as well, where they could be safely stored at a wider range of RH and temperatures without risk of activating corrosion processes. But many more applications could be developed to enhance the value of SCF treatment plans, for new and legacy collections in a wide range of areas.

4.1. Assessment of long-term effectiveness and polymer selection

There are thousands of polymers from which to choose for conservation of particular objects. Acryloid/Paraloid™ B-72 is very stable, which we found in our own simulations and reinforced in the literature. Conservators have some concern that this polymer exhibits solvent retention (studies cited in Davidson and Brown 2012, 100), where under ambient conditions, the rapid evaporation of solvent near the surface permits thin films to form which then act to retain remaining solvent in trapped bubbles (Li 2006, 286). Because of the rapid evaporation of acetone in ambient conditions, samples also sometimes exhibit "reverse migration" where the

polymer is drawn back out to the sample surface as it dries (Davidson and Brown 2012, 102-103). In established experiments with vapor and vacuum chambers, this problem can be mitigated effectively. As the samples in this study were impregnated using SCF, the polymer effused evenly throughout the objects and samples appear thoroughly impregnated. With the techniques described above for quantitative measurement of impregnation, more tests will reveal whether or not reverse migration occurs during decompression and the volume (if any) of uncured polymer or residual solvent trapped inside the object.

Li (2006) demonstrated that under certain conditions, Paraloid™ B-72 can become a culture medium for biological growth leading to subsequent biodeterioration. Most forms of carbon will serve as food for microorganisms, such as the carbon in residual acetone solvent trapped inside the microstructure decayed ferrous metal artifacts. Other forms of corrosion are essentially biodeterioration processes, where bacteria facilitate decay by creating chemical exchanges between a biofilm and a metal surface. Examples of this include when Sulfate Reducing Bacteria (SRB) form thin films over surfaces, converting sulfate ions into iron sulfides. Iron Reducing Bacteria (IRB) do the same and significantly contribute to Green Rust formation, particularly for ferrous objects in moist soils over long time spans (Neff 2012; McNeil and Little 1999).

It is noteworthy that SC-CO₂ treatment enhances any effort to control bacterial and fungal growth. Luo (2002) cited studies that CO₂ SCF effectively killed bacteria. Even treatments under two hours in duration will kill *Escherichia coli*, *Staphylococcus aureus*, and *Aspergillus neomycin*, and will decrease by 99% the proportion of Bacillus bacteria in a sample. Targeted research is necessary in this area to assess the effects of SCF exposure, with various co-solvents, upon IRB, SRB, and other biological agents of concern.

Finally, because the B72 can be “reactivated” and softened for removal or reapplication, the treatment is considered reversible. This is significant, because not all polymer treatments are reversible and thus polymerization is a controversial practice within the conservation community. The clearest example of this controversy is the application of silicone oils to archaeological artifacts, particularly organic materials (most strongly advocated by Smith 2003). Yet even in these studies, Smith demonstrated that exposure to polymers in composite objects had no negative effect upon later attempts to conserve cast iron shot with traditional electrolytic techniques.

While many other polymers may be applied in SCF treatment, those soluble in acetone, like Paraloid™ B72, have a distinct advantage in use. Summarizing points put forth by Cretté et al (2012, 3), SC-CO₂ is a poor SCF solvent for water by itself. SC-CO₂ is a good solvent for non-polar molecules and some low weight polar molecules. Because SC-CO₂ has a quadrupole moment instead of a permanent dipole moment, polar molecules like water do not dissolve as readily into the solution, so a greater volume of CO₂ is required to diffuse the same quantity of water and the process takes more time. Teshirogi et al. (2001) demonstrated that amphiphilic solvents (such as acetone, methanol, and ethanol) that have good affinity for both water and carbon dioxide can greatly increase the efficiency of mass transfer in diffusion. The co-solvents reduce the volume of carbon dioxide required. While

Teshirogi et al. found ethanol to be the most effective solvent, acetone also worked very well. By contrast, Sousa et al. (2007) found co-solvent combinations of isopropanol and water in SC-CO₂ to be most effective at extracting dirt from textile samples.

Several studies have experimented with Polyethylene Glycol (PEG) in their work with wood because conservators have preferred this polyether compound to stabilize and impregnate waterlogged wood for many years. Conservators have used PEG for decades and have conserved hundreds of thousands of objects of wood, paper, leather, and other organic materials, including PEG solutions with corrosion inhibitors for waterlogged composite iron-wood artifacts (Bobichon et al. 2000). Most of these treatments produced excellent results. As Wayne Smith said in his review, however, many of those objects were conserved before technicians understood the advantages of preparing artifacts by freeze-drying, or before advances in PEG chemistry led to blended molecular weight treatments, or where the conservators' efforts simply resulted in poor outcomes. Bad treatment resulted in organic materials with badly altered color, "wet" surfaces, and large volume of "weeping" unbound PEG which damages artifacts and makes them difficult to exhibit or store (Smith 2006, 30-31).

Teshirogi et al (2001) worked with PEG#4000 in their study. Chaumat et al. (1998, 1999) experimented with various formulations of PEG solutions in their attempts to explosively inflate wood that shrank during previous drying and conservation treatments. Kaye, Cole-Hamilton, and Morphet (2000) found that using a SCF containing methanol, PEG could be extracted from conserved objects, leaving very little remaining in the objects. The implications of this are that conservators can use SC-CO₂ fluid with methanol as a co-solvent for extractions to remove PEG from poorly done past consolidations of wood artifacts, while using water SCF solutions to impregnate with new PEG when appropriate. Authors found they still needed to apply consolidants after treatment, finding success with Paraloid™ B72 dissolved in p-xylene (dimethylbenzene) yielding the best result.

Finally, Teshirogi et al (2001) also showed that a single step, two-stage process gave very satisfactory result, extracting the solvent and water while diffusing polymers into sample pores. As we found in our study, using a single treatment would dramatically increase the efficiency of the SCF process for artifact conservation. This will require new instrumentation set up in our lab that will allow us to adjust the composition of the SCF during the extraction, adding or removing co-solvents and/or chleating agents. We will also need to be able to draw off and characterize the SCF during treatment, measuring the extraction rates of chlorides, mercury, or whatever targeted compounds are being removed.

4.2. Structural Stability and Comparative Studies

The majority of studies applying SC-CO₂ extraction to archaeological materials has centered on organic materials, particularly various types of waterlogged wood. Wood is particularly challenging to conservators, because the decay of organic structure leaves the material fragile and subject to shrinkage, warping, and distortion. This happens because water replaces 60%-80% of the bulk of organic structural material in the cells of woody materials. If the water mass is then

removed, the loss of bulk results in shrinkage. By contrast, warping occurs in wood samples because of surface tension. The cohesive surface tension of water (or liquid consolidant) in each cell or void forms a meniscus resistant to capillary action, while at the same time phase transitions (mostly as evaporation from surfaces) cause osmotic pressure to move fluid through the object's cellular structure (Luo 2002). The tensions between osmotic pressure and surface tension causes warp. This is exacerbated when the material, like cork, includes hydrophobic properties. Because both decay and water replacement of bulk is always irregular throughout an object, these changes cause increases in tension between surfaces that lead to cracking and differentially distributed warp depending upon the orientation of the grain, location and extent of decay, and other structures. Traditional treatment of waterlogged wood, along with most other organic materials, involve baths to which slowly replace water with a solvent like methanol, while also extracting salts and introducing biocide or fungicide when needed, then replacing the solvent with a bulk stabilizer. As discussed above, PEG has become the most popular group of stabilizers. While these studies do not provide perfect models for the applications under consideration here, the number of studies applying SCF extraction and their varied success makes their review useful.

Conservators' pursued experiments with SC-CO₂ applications to address two main concerns: faster processing times and increased penetration of PEG into objects. They have assessed outcomes by examining the quantity of PEG impregnating objects or samples, color alterations, strains and stresses created during treatment (assessed by deformation outcomes), and weight change to objects. Because SCFs have no significant surface tension, the treatment should be more gentle on waterlogged wood than other types of drying, despite the changes in overall pressure.

These studies generally revealed that using SC-CO₂ to only extract water from objects yields results that fall between freeze and open air drying, including good color and texture preservation, but moderate shrinking, cracking, and warping. Schindelholz et al. (2007) and Schindelholz et al. (2007) presented a comparison between simple air drying, freeze drying with PEG impregnation, and supercritical drying. Their findings were unsurprising. Air-dried samples suffered worst cracking, warping, and shrinkage. Both freeze-dried and supercritical-dried samples exhibited some cracking and warping, and at times, the supercritical samples shrank more than freeze dried samples. Air and supercritical drying preserved surface color, while the PEG impregnation darkened surfaces. Investigators could not determine if that shrinkage had occurred during the methanol exchange treatment or during supercritical treatment. More to the point, these researchers made a comparison between one technique that included replacement with a bulking agent (freeze drying with PEG) and two techniques that did not (air and supercritical drying). In a similar study, Cretté et al. (2012) applied SC-CO₂ drying with methanol as a co-solvent to dry artifacts of cork, which is notoriously difficult to conserve. They did not use PEG or another bulking agent and also found 2%-4% shrinkage in all directions, along with a shift to lighter colors in dried surfaces.

When SC-CO₂ processes have been used to extract water *and* impregnate samples with a bulking agent, however, the results are generally excellent,

comparable to other best practices, and dramatically faster. Studies find that 12-24 hours of SCF treatment roughly equate to 18 or more months in bath treatments at ambient conditions (Couéré 1998). Teshirogi et al (2001) found ~1% tangential shrinkage using PEG 4000. Coeuré et al. (1998) tested PEG 400 and PEG 4000 and found no significant shrinkage. Kaye and Cole-Hamilton (1994) and Kay, Cole-Hamilton, and Morphet (2000) tested cork, bone, bark, antler, pinecones, rope, and composite artifacts (including ferrous metal with wood and/or bone). Their tested wood samples experienced shrinkage rates between 3%-6% with a mean of 3.3% and cracking occurred on 21% of wood specimens. Significantly, supercritical dried artifacts showed no additional shrinkage or change in dimension, even when stored for five years in uncontrolled environmental conditions in a lab.

Some studies have pursued other questions, such a Chamut et al. (1999) attempt to swell wood samples that had previously lost volume when drying. They found promising results when they used rapid decompression of 15-minute SC-CO₂ treatments. D'Andrea et al. (2003) got good results using the technique to dry "hard" and "soft" waterlogged bone material from an Italian site from the Neolithic, using SC-CO₂ with methanol as a co-solvent. While the weight change due to water loss was expected and the authors mentioned no warping, delaminating, or noticeable shrinkage, they stated that the technique did deform or obscure traces of use-wear on the bones, particularly what we presume to be microscopic traits of cut marks. The authors did not elaborate on this beyond a brief mention in their conclusions.

4.3. Changes to mineralogical structures upon dehydration

One area requiring more examination is the effect of SCF treatments to the microstructure and other characteristics of iron, steel, ferrous metal and composite objects. These metallurgical characteristics are a function of temperature, pressure, and time. If this technique is to be determined ethical as a method to stabilize, consolidate, and seal corroded objects, then research must demonstrate that exposure to these high pressures does not change the microstructure or properties of the metal, or at least show that the changes can be identified and determined acceptable trade-offs for effective conservation. The microstructure is key to the properties of the object, such as its hardness, and can reveal clues as to manufacture and use in an object's life history, so its preservation (when possible) is essential. A mineral form like martensite, for example, is an indication of quenching in carbon steel. Gerhard Eggert expressed concern that this structure may be disrupted by heat treatments in conservation, with temperatures as low as 180°C. His concern was echoed by others in discussion (Selwyn 2011, 50) and is a distinct thread in conservation literature generally (Schmidt-Ott and Boissonnas 2002). The SC-CO₂ extractions conducted in this study were done *at least* 40°C below the *most conservative* critical temperature points identified in the literature.

The subcritical studies discussed below in section 4.4 demonstrated that those treatments caused irreversible changes in the mineralization structures on corroded iron artifacts. deViviés et al. (2007) showed that subcritical fluid treatment activated changes in the structure of corrosion mineralizations, where akaganéite and lepidocrocite reformed into hematite. After observing color changes

in the corrosion products, shifting from light ochre tones to red tones during subcritical treatment, González-Pereyra et al. (2010, 50) undertook a Micro Raman Spectroscopy analysis of subcritical treated artifacts and revealed only goethite, hematite or magnetite. This suggested that if any lepidocrocite, akaganéite, or other less stable phases of corrosion product had been present, they were transformed by subcritical treatment into more stable phases, consistent with deViviés et al. (2007). Other studies applying subcritical treatments have also observed these changes, including changes from lepidocrocite and magnetite observed as localized color change from orange to black (Näsänen et al. 2011).

Neff (2012, 41-42) argued that the subcritical dechlorination processes developed by Clemson's WLCC team is promising, but scientists need to understand the actual effects on the chemistry, structures, and morphology of the corrosion products before the technique can be applied more widely. The chemical and structural changes of the corrosion products, such as the phase transformations, must be mapped (as in this study) and understood if conservators are to understand the parameters controlling the kinetics of dechlorination and apply the technique widely. Neff has formed a collaboration with researchers at PME and A-Corros to determine the parameters of mineralogical changes, optimize the subcritical treatment process, and further clarify the evolution of the corrosion products so that the technique can be applied on an industrial scale. That work is ongoing.

Wang (2005) experimented SCF extraction with hydrated inorganic compounds, including ferrous compounds, measuring mass loss during extraction. His key finding was that almost all hydrated mineral species lose their water during SC-CO₂ extraction and results suggested that almost all physically or chemically bonded water can be extracted with supercritical CO₂. The author was able to demonstrate significant mass loss from these compounds: FeCl₂•4H₂O; Fe(NH₄)₂(SO₄)₂•12H₂O; FeSO₄•7H₂O; Fe(NO₃)₃•9H₂O; Fe(NH₄)₃(SO₄)₂•6H₂O. In addition, Wang showed that ferrous sulfate dehydrates in supercritical treatment, while iron heptahydrate/ferrous sulfate (FeSO₄•7H₂O) dehydrated more effectively by SCF extraction than thermal treatments, under the proper conditions.

Since water can be extracted from iron hydroxides and oxyhydroxides with SCF, do these dehydrated compounds then form stable anhydrous ferric oxides, like alpha-phase hematite, gamma-phase maghemite, or magnetite? These changes are similar to the mineralogical shifts in subcritical treatments. Experiments will be required to assess these changes, as well as to assess the effects of these changes on artifacts, including mass loss, increases in porosity in the corrosion layers, changes to the structure of the corrosion product, and any resulting increase or decrease in the strength of adhesion among corrosion layers and remaining iron.

4.4. The problem of extracting chlorides and salts

The application of subcritical and supercritical fluid treatments hold great promise as batch treatments that can accelerate the extraction of chloride salts from ferrous metal artifacts. As discussed above, the keys to slowing or stopping decay of ferrous metal artifacts are dehydration (removal of liquid or vapor water, or weakly bonded water that can become available for reaction), stopping biological growth, retarding the movement of electrons (to inhibit reactions), and removing or inactivating

highly reactive free Cl^- ions and bound chlorides. Thus far, our work has centered on the first and thus third issues. While our work was not intentionally directed at inhibiting bacteriological or fungal activity, SCF treatments fundamentally inhibit those processes. Chlorides present the final, and frankly, the most daunting challenge.

North and Pearson also pioneered traditional methods for extracting chlorine. Since 1975, the practice has involved using sodium hydroxide solution (0.5 mol/L, pH 13.7) containing 0.5 mol/L sodium sulphite, heated up to 70°C and stirred. After treatment, the chemical agents are washed out thoroughly and residues are precipitated with 0.1 mol/L barium hydroxide. Drying is achieved using acetone. The technique is slow and involves lots of caustic chemicals (Schmutzler and Ebinger-Rist 2008).

Building on the pioneering work of N. A. North and C. Pearson cited above, Lyndsie Selwyn and her colleagues have established more detailed understanding of the chaotic diffusion of chlorides into and out of archaeological iron. (Selwyn 2004, 294-306; Selwyn, et al. 2001, 109-120; Selwyn, et al. 1999, 217-232). The extraction of chlorides relies upon different concentration gradients drawing of chlorides to diffuse into the bath solution. This can be accelerated when hydroxide ions (OH^-) are also in the bath solution, since Cl^- will exchange with the (OH^-) in molecular arrangements. But for this to happen, an excess of hydroxide must diffuse into the object, activate the reaction, then the liberated chloride must diffuse out, often along “tortuous” paths through pores and interstices among corrosion layers, metal, and concretions, many of which can act as membrane-like barriers that interrupt the diffusion process by cohesive surface tension discussed above (Näsänen et al. 2011, 2).

Over the past decade, Warren Lasch Conservation Center (WLCC) researchers have published a series of experiments extracting chlorides using *subcritical* fluid treatments on hundreds of diverse artifacts and test specimens. This team has been using alkaline solutions raised to temperatures above 100°C and pressures above 30 bar, a region where water is above its normal boiling point, but remains a liquid instead of gas or vapor. By working at subcritical combinations of pressure and temperature (for water), the WLCC collaborators can “tune” the properties of water to use new thermodynamic and kinetic options and chemical paths unavailable in simple diffusion treatments in ambient (a.k.a. “atmospheric” conditions. In the subcritical region, water and water solutions exhibit lower viscosity, surface tension, and when using these temperatures, density. These changes improve water’s behavior as a solvent and increase it’s ability to penetrate pores and interstices. The changes enable the researchers to use lower concentrations of $\text{Na}(\text{OH})$ in their solution. (Näsänen et al. 2011). Their results also suggest that the pressure and temperature treatments convert akagénite and lepidocrocite into hematite, which is more stable and less reactive (deViviés et al. 2007; González-Pereyra et al. 2010).

The WLCC staff have used subcritical treatments to shorten the salt extraction time to an average of 15 days (González-Pereyra et al. 2010, 39), where traditional treatments would have taken as many weeks or months. Their tests show consistent removal of all detectible chloride from objects, including interior

pores, where they detected no chlorides but identified sodium residue from the Na(OH) solution, which they argued represented proof that the solution and extraction had entirely penetrated the artifacts. As a consequence of the treatment, the objects showed no active corrosion signs after two years of open storage. This remained true, notably, even without protective coatings preventing moisture reabsorption (González-Pereyra et al. 2010, 45-50).

Perhaps most importantly, the many studies undertaken by WLCC researchers clearly indicate that subcritical treatments allow safe and rapid chloride extractions from concreted artifacts, removing the salts and chemically stabilizing entire nodules. This is complete before any other cleaning or conservation work is undertaken, without negative impacts upon the cohesion of the layers of corrosion products or the adhesion of those layers to the remaining metal core (González-Pereyra et al. 2010, 39-40). Irreversible changes to the color of the corrosion products is perhaps the only negative effect, and this is inconsequential as an effect of stabilization. This drawback is far outweighed by the benefits derived from post-treatment deconcretion and mechanical cleaning of the corrosion matrix, which can be done at a slower pace with a dry object (Näsänen et al. 2011).

The WLCC staff are currently experimenting with combinations of subcritical and supercritical treatments to see if the process could include the application of tailored corrosion inhibitors and consolidants in a single step treatment (Näsänen et al. 2011, 20-11; González-Pereyra et al. 2010, 49), essentially what we have done in the present study.

While this was not part of our experiments to this point, supercritical fluid treatments could be tailored to extract chlorides, at least by testing Na(OH) as part of the SCF solution. More importantly, with a specifically designed SCF, all chlorides could be removed. Wang (2005) asserted oxyhydroxides can be dehydroxylated with SC-CO₂, presumably including the chloride hosting mineral akagenéite (β -FeOOH). Akagenéite often forms at the corrosion interface between existing products and the remaining iron surface and can form very quickly if saturated iron samples containing chlorides are allowed to air dry⁴ (Cook and Peterson 2005). The chlorides held within its crystal lattice are notoriously difficult to extract by established and ethical mechanisms, and the mineral reactivates anywhere above 15% RH. Current theory states that the surface hydroxyl groups on β -FeOOH will chemisorb or physisorb atmospheric water that then dissolves the surface-adsorbed chloride to produce an electrolyte, thus leading to additional corrosion of iron in contact with the akagenéite in the material (Watkinson and Lewis 2005). As mentioned above, the dehydroxylated mineral will presumably form into a more stable ferric oxide, but this must be determined.

A SCF could be optimally configured to extract chlorides, including free ions, those held within crystal structures, and perhaps even those bonded to iron as ferric chloride (FeCl₃). Pure carbon dioxide is a weak solvent for metals, however, so no

⁴ It is worth noting that as recently as 1994, many archaeologists still debated whether wet iron artifacts recovered from the field should be dried before packing them to be shipped to the lab (Sease 1994:66).

metals are extracted in pure SC-CO₂. By adding complex agents, the SCF becomes a much more efficient solvent for metals. In his simulations of Martian soils, for example, Wang (2005, 87) used a small amount of water with the co-solvent chelate⁵ as the fluid to attempt SC-CO₂ extraction of metals. Wang showed that Mg²⁺ could be extracted from MgCl₂. Similar experiments could be conducted with ferrous and ferric chloride powders, using an appropriate SCF.

SC-CO₂ (or alternate SCF) extraction may offer some critical advantage over sub- or near-critical treatments. Our extractions were conducted at 60°C, below those used in the subcritical extractions at WLCC. With longer soaking time at peak pressure, the temperature could even be run at room temperature, remaining below temperature thresholds that might prompt changes to the metallurgical structure or hardness of the artifacts.

4.5. Extraction of hazardous and volatile compounds

Industrial archaeologists, conservators, and the managers of industrial heritage should note that SCF extraction also holds great promise as a method to remove hazardous compounds from artifacts. In our proposal for this work, we wrote that we hoped to extract water from corroded iron objects while leaving dirt and grime intact. Among the reasons for this, oil stains and grease are often important to the life history of tools, machine parts, and industrial heritage objects made of ferrous metals. To a certain extent, this technique can be tuned to minimize or maximize the extraction of hydrocarbons. Our research into comparative studies of the solubility of machine oils and grease using SCF showed that the technique can also be used to remove toxic compounds from industrial and other cultural heritage materials, where environmental pollution or contaminants threaten human health and safety.

Because of the conglomerating tendency of industrial production, heritage scientists know that sites are sometimes contaminated with hazardous or toxic residues. These compounds can also migrate in ground water among nearby sites within a watershed, spreading post-industrial contamination to sites from all time periods in an area. The contamination often presents ethical challenges to archaeologists and heritage professionals because remediation comes into conflict with preservation. The remediation of toxins preempts heritage preservation.

SCF treatments can extract, neutralize, and/or encapsulate many of these contaminants. Contaminated artifacts must often be cataloged on site during remediation and then disposed of, along with the other contaminated soils and debris. Objects that are part of existing legacy collections are sometimes found to be contaminated and must then be disposed of as hazardous waste. Curating contaminated objects would present too great a risk to current populations when balanced against their cultural significance. Among contaminated collections, most pre- and non-industrial heritage artifacts absorb contaminants from their post-depositional context. For the objects of industrial heritage, however, the residues of contamination can often be part of the life history of the artifacts that conservators

⁵ Chelate as a ring-structure compound where ligand molecules bond with a metal ion on two or more sides, in this case, a high performance perfluoropolyether.

would otherwise find they were ethically obligated to preserve *in situ*. The SCF technique should be considered an important tool in making these decisions.

SCF extraction can be tuned to remove a wide range of compounds. While not conducting experiments related to conservation science, Wang (2005, 12)) summarized some industrial applications, where SCF of CO₂, Propane, and Benzene have been used to extract petroleum, oil, asphaltum, and nicotine residues; bean and sunflower lipids; essences of black pepper, hops, and pineapple; as well as lemon, corn, fennel, cinnamon, and almond oils. Given industrial applications, it is not surprising to note that conservators have shown that SC-CO₂ extraction can be tuned to remove a wide range of molecules from their diffused state within an object's microstructure. Rowe et al. (2013) showed they could extract a polyglycerol-based polymer and fatty acid moieties (methyl ester derivatives) that may have formed in a reaction between mummy-embalming materials and their SC-fluid mixture, in addition to beeswax, coconut oil, frankincense, glycerol, and humic acids in varying amounts.

Kaye, Cole-Hamilton, and Morphet (2000) examined extracted solutions from maritime artifacts using Gas Chromatography-Mass Spectroscopy (GC-MS) to measure the extracted compounds. The results showed that extracts contained vanillin, syringaldehyde, beta-sitosterol (a wood steroid), numerous long-chain fatty acids with up to 18 carbon atoms, and terpene dehydro-abietic acid.

Scientists and engineers have highly developed techniques to extract organic molecules, but by comparison, the extraction of inorganic and metallic compounds is comparatively new. Yet since the 1990s, the introduction of complex chelating agents in SCF has inspired a flurry of research in this area. Scientists have extracted organic and inorganic mercury from soils and solid materials (Wai et al. 1993; Issaro, Abi-Ghanem, and Bermond 2009). They have also decontaminated soils containing Naphthalene (Smyth et al. 1999) and PCBs (Yak et al. 1999). Many publications in environmental chemistry discuss extraction of aliphatic compounds, carboxylic and other acids, several pesticides and herbicides, fertilizers, and various phenols. SCF process can already be deployed on an industrial scale for the remediation of contaminated soils (Cocero, Alonso, and Lucas 2000).

Some conservators have used SCF to extract toxic materials from collections, where compounds had been added to preserve organic materials under older museum practice. These legacy collections present problems because now the dust from these objects presents unacceptable threat to human health for museum staff and visitors. Kang, Unger, and Morrell (2004) ran experiments to show that DDT (dichlorodiphenyltrichloroethane) could be extracted from wooden test blocks with various coatings, resulting in very slight variations in surface color. Consistent findings were reported by Tello, Jelen, and Unger (2005), who used contaminated collections from the Ethnological Museum of Berlin, sampling leather, fur, hair, hide, skins, feathers, hair, woven textiles of wool and cotton. They measured their content of arsenic, mercury, DDT, lindane (γ-hexachlorocyclohexane), and PCP (pentachlorophenol), and performed SCF extraction, using SC-CO₂ with ethanol as a co-solvent (also sometimes with trimercaptotriazine (TMT) as a chelating compound). The outcomes were excellent, where they removed 70%-90% of the mercury, 80%-100% of the DDT, 50% of the arsenic, and 60%-90% of the lindane.

Conservators can apply SCF extraction to contaminated cultural heritage, but the approach cannot be standardized. Each site or collection will present unique and specific contaminants requiring equally unique and specific SCF extraction. Technicians will choose their fluid, solvents and co-solvents, chelating compounds, temperature, pressure, and extraction times according to the needs of each case. Heritage managers must become aware that SCF extraction is one potential solution to toxics so that they will not assume that disposal or destruction remain the only options during remediation projects.

4.6. Corrosion assessment

Professional curators and heritage managers will need some non-destructive testing options to monitor the effectiveness of treatments over time, perhaps without removing the corrosion nodules or layers. In section 3.2.2 above, we outlined two methods for destructive analyses yielding quantitative calculations to assess the penetration of polymer into samples, using either optical microscopy with epifluorescent illumination of void analysis or SEM EBS using a vapor stain like Ruthenium Tetroxide (RuO₄). In their study assessing the outcomes of conservation practices from Winchester, England, Keene and Orton (1985, 30) remarked that it would have been useful if they could have systematically compared radiograph images of corrosion nodules and mineralized objects with iron cores. Radiographs before and after treatment and then repeated after the objects had spent decades in storage would have allowed them to systematically examine the effectiveness of treatments attempting to stabilize corrosion layers over an iron core while also preserving the corrosion layer in place. This type of assessment will be essential as the techniques discussed above are applied to stabilize corroded nodules from maritime and chloride-bearing terrestrial environments.

Established technologies now allow for the direct assessment identified by Keen and Orton, which might follow the structured light scanning or 3D modeling done by other researchers, but also mapping object's internal layers. Researchers will need to establish a method to map changes to artifact structures using something like multiscale X-ray Computer Tomographic (CT) imaging to build high-resolution 3D visualizations of corroded iron layers that allow identification of changes over time. This type of work is already underway at laboratories like that of the New Techniques for Ancient Materials research group led by Prof. Claire Gervais at Switzerland's Bern University of the Arts⁶ (c.f. Jacot-Guillarmod et al. 2015).

4.7. Scaling up the process/work in the field

While working in the Michigan Tech lab, we were very limited by the size of our pressure bomb. If this technique is to become a normalized practice done widely in the field, the process must be scaled up to a true batch operation with both scale and mobility. While many questions remain to be addressed before SCF extraction can be systematically applied, existing literature already demonstrates that the technique will work to treat large artifacts or batches of objects.

⁶ <http://www.gervaislab.ch/research.html>

Our team discussed how the process could be scaled up. Does the increased energy and materials demand of larger scale processing make the technique unrealistic and cost-prohibitive? If the equipment could be made mobile, and a cooperative effort made among a large number of institutions, could the cost of setting the system up be measured against cost savings in treatment collections?

There are several options, including:

- i. an institution like Michigan Tech or the WLCC could acquire an industrial-scale composite extraction autoclave and begin receiving large-scale objects or large collections for treatment, delivered to a site like Houghton. Industrial autoclaves are readily available, but expensive.
- ii. a collaborative organization or consulting company could purchase a mobile composite extraction autoclave that can be moved from facility to facility. Such devices are already manufactured for biohazard waste treatment, although they more expensive than stationary models.
- iii. designing a subterranean or semi-subterranean system that could be cheaply built on a site using reinforced concrete. Experts could assemble the system on the grounds of a museum or an archaeological site, then demolish the chamber when the work was complete while taking key parts and equipment to the next site. This would remove the need to transport a large pressure tank between jobs and could perhaps be less expensive. Developing this system would require much more research.

Michigan Technological University's multidisciplinary educational programs, including Senior Design and Enterprise, are ideally suited to examine these options. In these programs, a group of students from different departments could design these systems and develop cost-benefit analyses for them while supervised by professional engineers and faculty.

5. Conclusions

Supercritical Fluid Extraction using SC-CO₂ is a useful and effective way to dewater and stabilize batches of encrusted ferrous artifacts from industrial heritage sites. The technique is faster than traditional treatments—faster by several orders of magnitude. Where a cannon may spend 4 years in traditional treatments, a well-tuned SCF extraction might conclude in 4 days. The stresses introduced upon objects by the treatment are no more damaging than ongoing, active decay or any other existing treatments to stop corrosion. The procedure can be reversible, in the sense that the treated objects are stable for long-term curation or the polymer can be removed for more detailed interventions at some point in the future. The compounds used are all quite benign and while the operation of equipment at supercritical pressures requires special training, the process is green and safe to humans. While much work remains to be done to determine optimal polymers, selections of solvents and co-solvents, and extraction of chlorides and toxic compounds, the SCF technique is very promising.

Team members designed and executed formal conservation treatments for 32 objects in all during this study. Twenty ferrous metal artifacts were conserved using traditional techniques, while ten artifacts were subjected to systematic SCF

treatments and follow up assessments. Two additional artifacts were treated and added to the comparative collection curated at Michigan Tech, where they can be examined as part of the diachronic study of outcomes. Student teams completed all the work, researching, designing, and executing treatment plans while supervised by faculty mentors. The students and faculty wrote a research blog about the project, but after speaking with consulting conservators, we were advised to finish the reports and publications before posting the blog entries. Those public postings are pending.

This study established a robust collaborative relationship surrounding conservation and corrosion science at Michigan Technological University. A group of eight undergraduate and graduate students from the departments of Social Science, Materials Science and Engineering, and Chemical Engineering engaged with this project over three years (2012/13-2014/15), learning about conservation science and ethics, and presenting their findings at campus events and at the Midwest Archaeology Conference (Atkinson et al. 2014a) and the Midwest Historical Archaeology Conference (Atkinson et al. 2014b). From that group, one student went on to develop an undergraduate thesis on metals conservation, won 3rd place overall at the 2015 Undergraduate Research Expo, and has made application to graduate schools to begin a MS program in conservation science and archaeology. Faculty presented findings at two major conservation meetings, BigStuff 2015 (Scarlett 2015) and the Grupo Latinoamericano de Restauración de Metales (Scarlett 2014). A version of those presentations is under review for publication in the proceedings of the BigStuff meeting and several other targeted articles are in preparation for industrial archaeology and industrial heritage journals.

The faculty learned a great deal about collaborations from this project. We have since extended our collaborations to others in the Department of Materials Science and Engineering and the Department of Chemistry, mentoring student investigations of silicone oil treatments of archaeological leather, for example. Faculty have also initiated discussions about core facilities improvements at Michigan Tech, identifying ways to expand our capacity for supercritical chemistry and conservation by adding an industrial scale autoclave to our facilities and seeking support for post-doc researchers in conservation science.

As a final outcome, the researchers have contact with professional conservators and scientists at A-Corros, The Warren Lasch Research Center at the Clemson University Restoration Institute, the Archaeological Preservation Research Laboratory at Texas A&M University, and the German Mining Museum. We look forward to collaborations with these scientists as we seek funds to support the ongoing work to develop SCF conservation, enhance our own core facilities, mentor students into graduate education and conservation careers, and provide conservation services to the heritage institutions in our region.

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benefited by conversations with Philippe de Viviés and Paul Mardikian at BigStuff 2015. Our experiments and our insights into conservation science were greatly improved as a result of these interactions. As always, any errors herein are our own.

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