



## Introduction

Archaeological excavation of USS *Monitor* (1862) recovered over 200 tons of material, a significant proportion of which is grey cast iron. The largest grey cast iron objects are the ship's two, XI-inch Dahlgren shell guns, alongside many structural, engine, condenser, and pump components. Small cast iron objects from *Monitor* can be graphitized through the full thickness, and objects retaining a metal core typically have a graphitized exterior layer of at least 5mm. The scale and relative fragility of these objects necessitates testing of conservation treatments, particularly with respect to their effects on the physical integrity of the graphite layer.

Destructive testing on archaeological materials from *Monitor* is limited, thus requiring preliminary experimentation on simulated archaeological material. In order to adequately test treatments before they were required, it was necessary to find a method to generate samples which required less than 6 months to complete, using only readily available equipment and materials. This poster discusses the process used to create simulated graphitized cast iron samples

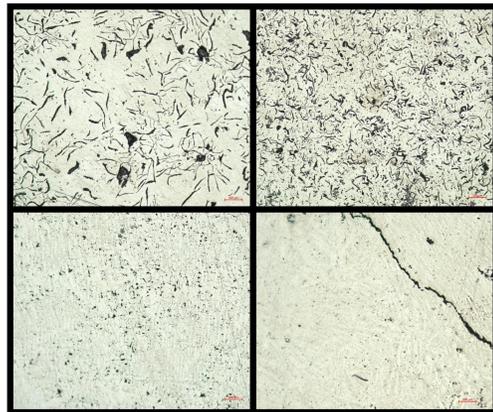


Figure 1: Clockwise from top left: Civil War Hotchkiss bolt, ASTM A48 Class 20, recycled cast radiator, ASTM A48 Class 40.

## Identification of Sample Materials

Metallographic analysis was used to determine a starting material for creating test analogs of US Civil War era grey cast iron. Three potential test materials were sampled: a nominal grey cast iron scrap (re-cast from 20<sup>th</sup> century radiators), ASTM A48 Class 20 [C20] grey cast iron (from weightlifting equipment), and ASTM A48 Class 40 [C40] grey cast iron (18.4mm diameter extrusion cast round stock). For comparative purposes, an unprovenanced 4.5" Hotchkiss bolt was sampled, and used along with information published by Caporaso et al (2008). Samples were epoxy-mounted and ground to 0.05µm using a Buehler Phoenix 4000 sample preparation system, following the manufacturer's instructions for ferrous alloys. Immediately before viewing, samples were hand polished using 3 micron diamond abrasive on a felt pad.

The scrap radiator material was identified as white cast iron and discarded. Following terminology in ASTM A247-17, the graphite in the Hotchkiss bolt is predominately oriented in a type B distribution, C20 in a type C distribution, and C40 in a type D distribution. Flake size differs substantially (see image 1 above) with smaller flakes in C40 than C20, and smaller flakes in C20 than the Civil War period Hotchkiss bolt. Neither modern alloy is a perfect structural analog of the sample from the Hotchkiss bolt, but both are acceptable. C40 is more readily available and easier to regulate sample size, and was therefore chosen as a starting material.

## Initial Degradation Methods

Two principle methods were identified for structurally altering the modern C40 alloy to better resemble graphitized, marine archaeological cast iron: submersion in acids, and electrolytic corrosion with applied current. The former was identified as an option based on protocols for iron digestion to analyze residual chloride, and the latter from published examples (e.g. Liu et al 2009, Weizhen and Chunchun 2005).

Ten samples were cut from 18.4mm diameter C40 stock, with 4.5mm +/- 1mm sample thickness. These were designated A-H and K-L, and subjected to HCl and HNO<sub>3</sub> at different concentrations (Table 1). Each sample was immersed in enough acid to dissolve 70% of the iron present in the sample if a 100% efficient reaction occurred. The goal was removal of 30-50% of iron by weight.

Eight samples at 7.1mm +/- 0.1mm thickness were subjected to electrolytic corrosion. These were submerged in 2% NaCl in DI water and subjected to current at variable amperage, beginning at 0.5Amps. Every 24 hours, one sample was removed and weighed. After the fourth sample was removed, the solution was renewed, and current turned off for 48 hours. When electrolysis was restarted, the current was reduced to 0.25A. Twenty-four hours after restarting electrolysis, the fifth sample (Q) was removed; an additional sample was removed every 24 hours thereafter until none remained (Table 1).

All samples were weighed and measured to allow tracking of their degradation.

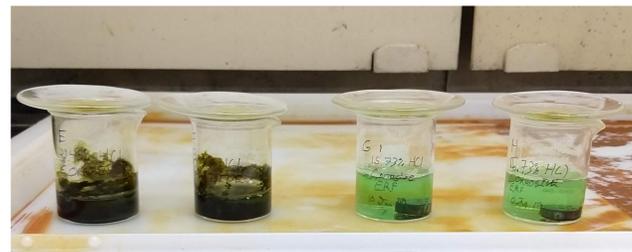


Figure 2: Samples E-H (left to right) after 4 days in HCl. E and F began dissolving immediately, releasing flake graphite which floated on the solution surface; by day 4 this had begun to gather in clumps on the sides of the beakers. G and H were the only acid degradation tests with a successful result

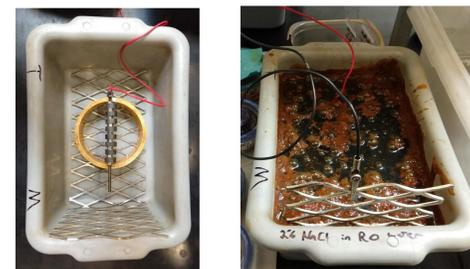


Figure 3 (left) and 4 (right): Setup for electrolytic degradation before testing at left, and after three days of applied current at right. An EPSCO D612-T DC power supply was used to provide current for the system.

## Preliminary Results

Results were considered successful if at least 30% of the starting mass of iron was lost, and no loss of sample volume was visible. Volumetric loss was not measured, as visually identifying small chips, although qualitative, had a finer resolution than available quantitative measurements.

Of the acid-degraded samples, only 16% HCl removed >30% of the starting Fe mass without visible volumetric change, taking 6 days to react. Electrolytic corrosion in 2% NaCl achieved a similar result in 3 days, and the rate of iron loss appeared more controlled and predictable.

All samples were x-rayed to determine if a solid metal core remained present. In addition to the quantity of iron lost, the distribution of loss is important in creating analog test samples; samples with a highly graphitized outer layer around a solid metal core will better reflect the structure of archaeological materials. Electrolytic corrosion gave superior results, and was chosen for full-scale sample generation.

Sample	Soln	Sample Mass (g)	Mass Fe (g)	Final weight (g)	Mass Lost (g)	Percent Lost	Time (days)	Volumetric Loss
A	68% HNO <sub>3</sub>	8.3507	7.8079	7.5335	0.8172	10.47	6	Yes
B	68% HNO <sub>3</sub>	8.2335	7.6983	7.4083	0.8252	10.72	6	Yes
C	17% HNO <sub>3</sub>	9.8813	9.2390	7.3522	2.5291	27.37	6	Yes
D	17% HNO <sub>3</sub>	10.1140	9.4566	7.562	2.552	26.99	6	Yes
E	32% HCl	9.0648	8.4756	6.1574	2.9074	34.30	6	Yes
F	32% HCl	8.8609	8.2849	5.8874	2.9735	35.89	6	Yes
G	16% HCl	10.2757	9.6078	7.1259	3.1498	32.78	6	No
H	16% HCl	9.4880	8.8713	6.508	2.98	33.59	6	No
K	17% HNO <sub>3</sub>	7.5090	7.0209	4	3.509	49.98	4	Yes
L	17% HNO <sub>3</sub>	7.2557	6.7841	3.9222	3.3335	49.14	4	Yes
M	2% NaCl	13.2369	12.3765	11.6541	1.5828	12.79	1	No
N	2% NaCl	13.3477	12.4801	10.4882	2.8595	22.91	2	No
O	2% NaCl	12.9098	12.0707	9.1005	3.8093	31.56	3	No
P	2% NaCl	13.1240	12.2709	8.2953	4.8287	39.35	4	No
Q	2% NaCl	13.0187	12.1725	7.798	5.2207	42.89	5	No
R	2% NaCl	12.6710	11.8474	6.6416	6.0294	50.89	6	No
S	2% NaCl	12.8343	12.0001	5.8056	7.0287	58.57	7	No
T	2% NaCl	13.1440	12.2896	4.9653	8.1787	66.55	8	Yes

Table 1: Sample information and preliminary results

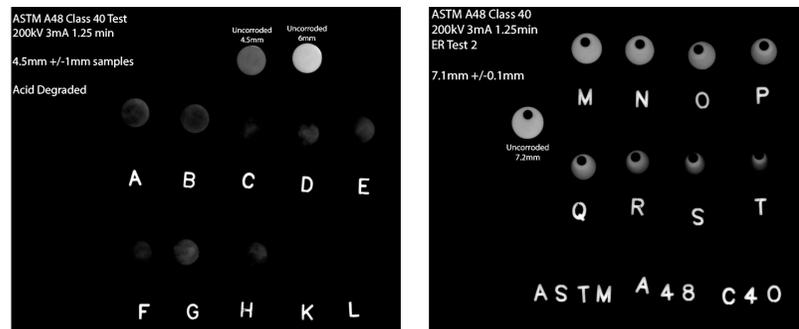


Figure 4 (far left): Radiograph of acid degraded samples showing distributed metal loss throughout the structure, with severity ranging from minimal to complete loss.

Figure 5 (immediate left): Radiograph of electrolytic corrosion samples. Degradation leaves a graphitized exterior layer with a solid metal core. Note that the metal core remains longest around the hole for the electrical attachment, and not in the center of the thickest area of metal. The electrical connection physically limits solution access to the surface, thereby protecting this area.

Figure 6 (Below) Electrolytic setup with 245 C40 tokens on a 316 stainless steel armature. Stainless steel mesh is just visible at the bottom of the tank, serving as the cathode.



Figure 7 (Below) Samples undergoing electrolytic corrosion.



## Sample Generation

After preliminary results were obtained, the electrolytic corrosion method was scaled up to begin creating 245 graphitized cast iron samples for future consolidation, corrosion inhibitor, and drying tests. Samples were split across seven #10, 316 stainless steel rods with a hex nut and washer between each sample. Each of the rods was sequentially connected to the adjacent rod, and the first rod connected to the power supply as anode.

Problems occurred with large-scale sample generation which did not occur in limited testing, resulting in a sample generation time of 60 days (compared to 8 days in small-scale). Because of the sequential wiring pattern, there were more electrical connections, and several of these loosened every time the platform was raised to remove and weigh a monitoring sample. Even with the connections checked and tightened daily, the rod with a direct connection degraded much faster than the six sequentially wired rods. After this was discovered the system was re-wired using a dedicated stainless steel connection to each rod, and this wiring remained in place until sample generation was complete.

Even with the wiring problems corrected, a higher amperage (2 amps) was needed to drive the reaction at a visually similar rate to the small scale tests at 0.5 amps. The large-scale setup had approximately 30x the sample mass, volume and surface area, but only approximately 15x more cathode and 10x more solution volume. These changes in proportion likely affected the reaction.

Because of scheduling conflicts and the unexpectedly slow corrosion rate, samples were checked less often at large scale. As a result, the experiment ran longer than necessary, resulting in weight loss equivalent to 60-80% of the original mass of iron (varying from sample to sample). However, the resulting sample materials were usable, with a defined graphitized layer around a solid metal core.



Figure 8: A sample from the full-scale generation, broken in half to show the structure. The exterior is fully graphitized. Below this is an iron-depleted layer which is no longer metallic, but is substantially harder and denser than the outer layer. At the center is a core of metallic cast iron.



Figure 9: A sample which has been cut rather than broken, showing the extent of core metal remaining.

## Future Work, Limitations, and Conclusions

Additional testing – notably SEM and XRD – is planned to clarify the structure of the samples, particularly at the metal-graphite boundary. Compressive force testing will also be used to compare the strength (and variations in strength) to that of de-accessioned spall from archaeological materials.

This testing was deliberately designed to use available equipment, and ideally to use inexpensive equipment which is widely available in marine archaeological conservation labs. Better volumetric measurement of samples, governing the reaction speed by current density, or using a potentiostat would likely create better controlled and more repeatable results.

Although there were problems in scaling up, this method was extremely successful in creating samples which are a useful structural analog for graphitized, marine archaeological, grey cast iron. By using a mixture of qualitative and quantitative methods, generating samples in this manner is possible even with extremely limited equipment: stainless steel hardware, a DC power supply, and a scale. Additional testing such as x-radiography is helpful, but the core method does not require it.

## Credits, Acknowledgments, and References

- All images are courtesy of The Mariners' Museum and Park.
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