Corrosion rate study of cannon at the Prince of Wales' fort

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Abstract

Prince of Wales' Fort near Churchill, Manitoba, Canada, has forty 18th century cast iron cannon set on its ramparts and exposed to the elements. Two hundred and fifty years of corrosion has removed historical detail. Although there is minimal pollution, (the neighbouring ocean has a low saline content and is frozen for much of the year), relative humidity is very high and windborne particles continually expose new material to corrosion processes. With the failure of numerous protective coating regimes, a fundamental re-examination of the problem of "preserving the cannons' fabric for future understanding, appreciation, and study" was initiated in 1996. Since no corrosion data for grey cast iron in a sub-arctic, marine environment was available to provide a scientific basis for resource management decisions, a thirty year corrosion rate study using coupons of like alloy has been instituted. Two questions have been posed in the study: what is the corrosion rate; and how long will it take at that rate to obliterate remaining surface detail? This paper presents the corrosion rate results for the first five years of the study. Also offered for discussion will be the question: what is an "acceptable" rate of material loss for cultural resources in an uncontrolled environment where access is difficult and visitation low?

Key Words: grey cast iron, cannon, atmospheric corrosion, sub-arctic marine environment

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Introduction

Prince of Wales' Fort is a large stone fortification constructed by the British between 1731 and 1772. It is located on a peninsula at the mouth of the Churchill River on Hudson Bay in Northern Canada. On the ramparts are forty, grey cast iron cannon manufactured between 1702 and 1760. These 6, 12, and 24-pounders still exhibit the royal cyphers, proof marks, weight marks, and astragals which anchor them in history. When the French captured the Fort in 1782, they disabled the cannon by spiking touch holes, blowing off muzzles, or knocking off trunnions. As a National Historic Site of Canada, the Fort commemorates the French-English rivalry in North America and the disabled cannon are valuable evidence of that rivalry.

Figure 1: One of forty cannon on Prince of Wales' Fort Ramparts

By the mid-1980's, the cannon exhibited an overall layer of corrosion with localized spalling. The edges of the markings were rounded from loss of material and the process was apparently continuing, albeit at a slow rate. As valued cultural resources, periodic attempts have been made to protect the cannon from corrosion. These were limited experimental treatments which it was hoped would lead to a conservation treatment strategy for long-term preservation of the collection. The various treatments included corrosion stabilization with ethylene diamine and coating with Tremclad® paint, coating with an aluminium mastic epoxy primer and an aliphatic catalysed polyurethane top coat, coating with an orthophosphoric acid metal conditioner, epoxy primer, and urethane acrylic enamel top coat, and finally coating with Conquest®, a tannic acid based solution with polymeric coating. Unfortunately, most of these coating systems have failed in large part due to the Fort's location. (Busse, 1997). The sub-arctic climate with relatively cold temperatures and high humidity year round means that most standard protective coatings developed for use in southern Canada are not appropriate.

The cannon are large artefacts with thick cross-sections of sound metal. They have survived over 200 years in their current environment with only minimal loss of surface metal and the markings are still legible. Considering this observation and the difficulty and expense of applying a protective coating to the cannon, questions were raised about the validity of the assumptions upon which the conservation treatment decisions were based. Perhaps the corrosion rate was so low as to be insignificant making expensive on-site treatments unnecessary. Was the rate of corrosion going to result in the future loss of information contained in the relatively shallow markings?

How far into the future would we have to consider: 100 years, 200 years, a 1000 years? In the next 100 years, would a conservator or conservation scientist develop a new protection plan which would effectively reduce any chance of further deterioration? Situated on a rocky, treeless coast without fresh water or electricity and only accessible by boat at high tide during the summer, all work at the fort is logistically challenging and expensive; and with shrinking financial resources, can the conservation of artefacts which appear to be barely deteriorating be justified? In addition, every time a new coating regime is tried, there is a risk of increasing the corrosion rate if the coating fails.

The cannon have been exposed to the elements since 1782 without a significant loss of material, particularly around the markings leading to the assumption that grey cast iron was relatively corrosion resistant in the environment of Prince of Wales' Fort. To confirm this assumption, a method of investigation had to be found which would not damage the cannon yet provide useful information. Corrosion rate data could provide this information, but no one has ever established a corrosion testing station at or near Prince of Wales' Fort. Data from Southern Ontario with its pollution and warm temperatures or Halifax with its marine conditions and pollution would not apply to Prince of Wales' Fort. In addition, the cannon are made of a grey cast iron alloy which has no modern industrial applications; and industrial scientists are not studying this alloy. In August 1989, Henry Unglik, Parks Canada Metallurgist, and Alex Barbour, then Chief of Marine and Industrial Conservation, Public Works Canada, visited the fort to study the cannon and obtain metal samples from broken trunnions. (Unglik and Barbour, 1992) One of their recommendations was to determine the corrosion rate of the untreated metal by establishing a corrosion testing station at the Fort using an alloy as close as possible to the cannon's grey cast iron. In 1996, a corrosion rate study was implemented.

The first step of the project was to define the objectives. Two questions were posed:

- What is the rate of corrosion for grey cast iron at Prince of Wale's Fort?; and

- Is the rate of corrosion for grey cast iron at Prince of Wale's Fort great enough to necessitate conservation intervention on the cannon?

The answers to these questions would be the foundation of future decisions concerning conservation treatments.

2. Method

This study determined the corrosion rates of grey cast iron test coupons by weight loss. Establishing a corrosion rate study is not normally part of a typical conservator's work in Canada. Fortunately, corrosion scientists have developed standard procedures. The test was based on the American Society for Testing and Materials (ASTM) G50-76, Standard Practice for Conducting Atmospheric Corrosion Tests on Metals (ASTM G50), and ASTM G92-86, Standard Practice for Characterization of Atmospheric Test Sites. (ASTM G92) The exposure times for the study were selected to find two corrosion rates – short-term (less than five years) and long-term (more than five years). The coupons were scheduled for retrieval after 1,2, 3, 4, 5, 10, 15, 20, 25, and 30 years.

The test coupons were made from a grey cast iron as close as possible to the cannon alloys. Unglik determined that the alloy was " typical of a phosphoric grey iron. It had a pearlite matrix with ferrite, a large quantity of graphite flakes and a considerable amount of iron phosphate eutectic" (Unglik, 1995) The closest modern alloy that could be poured in a small batch was "typical for grey cast iron. The structure consists of pearlite matrix with some free ferrite associated with graphite flakes and a small amount of iron phosphide particles evenly distributed." (Unglik, 1999) It was produced by McLean Foundry Ltd. of Brantford. Table 1 has a comparison of the alloying additions in both the cannon and the modern ingot. The higher silicon and lower phosphorus contents in the coupons will have them resist corrosion better than the cannon. On the other hand, the higher sulphur content will make the coupons more susceptible to corrosion. (Unglik, 1999)

Table 1: Analysis of cast iron coupons (Unglik, 1999)

Element	**Test Coupon Average of four coupons (wt. %)**	**Prince of Wales' Fort Cannon Samples (wt. %)**
carbon	3.1	3.7
silicon	2.0	0.7
magnesium	0.5	0.7
phosphorus	0.05	0.4
sulphur	0.17	0.05

The forty, rectangular test coupons are on average 105 mm wide, 152 mm long, and 6.7 mm thick. A thick coupon better simulates the thermal effects on the metal. Each coupon had an 18.5 mm hole drilled in each corner for mounting. An identifying number was stamped in the upper left corner of the skyward side. Each coupon was prepared to bright metal by air abrading with walnut shells at 60 psi. The surface was cleaned and de-greased using acetone. Several extra coupons were also prepared for use as controls for the mass loss analysis. Each coupon was weighed and then placed in Marvelseal 360 (aluminium foil and polyethylene laminate) pouches sealed with aluminium duct tape. Pieces of blotting paper were used to interleave the coupons. Each pouch also contained a sachet of dried, non-indicating silica gel.

The testing station frame is constructed of aluminium to which the coupons are attached with black nylon cable ties. The rack is angled at approximately 30 degrees above horizontal instead of the 59 degrees prescribed in the standard. It also faces 290 degrees NW instead of 180 degrees S (ASTM G50). Deviations from the standards could not be avoided due to location constraints. The skyward and groundward sides will have varying corrosion rates much like the cannon on the ramparts.

The coupon rack was installed on a modern, one-story service building located approximately ¼ km from the Fort. The rack sits on the roof, out of sight of visitors and passing marksmen. Figure 2 shows the rack installed. The ideal test site for the study was on the Fort's ramparts along side one of the cannon. However, the Fort is an interpreted historic site and site staff did not want a modern coupon rack situated beside the historic cannon.

The coupons were installed on August 9, 1996. The weather was 8º C with a light wind and a brief rain squall passed through leaving isolated raindrops on the bright metal. Spots of flash rusting quickly occurred.

Figure 2: Coupon rack installed on roof of modern building.

Climatic data is obtained from the local Environment Canada weather station located on the east side of the river. Unfortunately, there are limitations to using an unmanned weather station. The equipment tends to quit working during extremes in weather, particularly wind. Without a human on site, there is no data for these days. The station provides daily maximum and minimum temperatures, relative humidity, and precipitation. The severe climate makes it difficult to set up a weather station beside the test station. There is no electricity and it's too cold for long-term battery use. The inaccessible nature of the site means that batteries and sulphonation discs or candles cannot be changed on a regular basis. As a consequence, there is no time-of-wetness data because of these difficulties with maintaining equipment.

At each retrieval, four coupons are removed. They are immediately sealed in Marvelseal pouches with blotting paper dividers and a silica gel sachet. The exposed coupons and some control coupons are then shipped to the Analytical Laboratory at Parks Canada's Ontario Service Centre. The coupons from the first two years of the test were stripped of corrosion using the sodium hydroxide and zinc powder procedure from ASTM Designation G1-81, Standard Practice for Preparing, Cleaning and Evaluation Corrosion Test Specimens (ASTM G1). The method conformed to those proposed by D.H. Thomson (Thomson 1971). The coupons were suspending in a boiling aqueous solution of 20% w/v sodium hydroxide with zinc for five minutes. This method was found to be harmful to the laboratory equipment and dangerous for staff. For coupons from years three, four, and five, the safer electrolytic method, also described by ASTM Designation G1-81 and D.H. Thomson, was used. The electrolyte was a 5% w/v aqueous solution of sulphuric acid inhibited with Hostacor IT® and heated to 75 C. The coupons were exposed to a current of 24 amps at 4 - 6 volts for 3 minutes. For both procedures, control coupons were stripped at the same time to determine a correction value to allow for any metal lost during the stripping process.

3. Results

The climatic data was as expected for a sub-arctic location. The only months with average temperatures above 0º C, were June, July, August, and September for an average total of 112 days per year. The bay was frozen for approximately eight months every year. There were an average of 67 days with more than 0.2 mm of rainfall and an average relative humidity above 70%. (Environment Canada, 2004) The concentration of chlorides and sulphates found at the fort was low. According to Unglik (Unglik, 1995), the water trapped in the cannon bore contained <3 parts per million (ppm) chloride ions and < 30 ppm sulphate ions. The rainfall captured around the fort area contained < 0.1 ppm chloride ions and < 1 ppm sulphate ions. The Churchill River introduces fresh water into Hudson Bay, reducing the salinity of the bay water. The waters surrounding the peninsula had salinity of less than 20 parts per thousand (Green, Singh, Hicks, and McCuaig, 1983). For an outdoor display of metal artifacts, Prince of Wales' Fort has a relatively benign environment.

To date, the first five years, or short term, coupons have been retrieved. They were visually examined and photographed to note the surface condition before stripping. The coupons from years one and two had a uniform distribution of corrosion without any pitting. The skyward sides had a mottled appearance – dark brown with light brown spots. The groundward sides were mostly dark brown.(Stewart, Sergeant, and Unglik, 1998) For years three, four, and five, both sides were mostly dark brown with a uniform distribution of corrosion and some pitting. The amount of corrosion products was similar on both sides. (Sergeant and Stewart, 2001) The appearance of the skyward and groundward sides of coupon #5 both before installation and after five years exposure is shown in figures 3 and 4. After stripping, there was some pitting due to aggressive nature of the electrolytic solution and the insufficient protective action of the Hostacor IT inhibitor.

Figure 3a

Figure 3b

Figure 3: Skyward view of coupon #5 before installation and after five years on the rack.

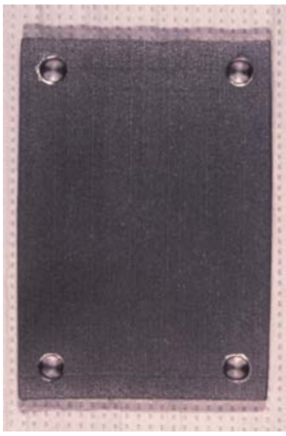

Figure 4a

Figure 4b

Figure 4: Groundward view of coupon #5 before installation and after five years on the rack.

The results of the mass loss analysis and corrosion rate ± one standard deviation are shown in Table 2. The mass loss was calculated using:

mass loss (g) = initial mass (g) - final mass (g) - correction (g)

The corrosion rate was calculated using:

$$\text{corrosion rate} = \frac{K \times W}{A \times T \times D}$$

where K = constant = 8.76×10^7 ☞m/year
W = mass loss (g)
A = Area (cm^2) based on the top, bottom, and sides minus the holes
T = exposure time (hours)
D = metal density of 7.17 g/cm^3

Over the five years of the study, the corrosion rate has dropped from an average of 14.5 ± 0.5 µm/yr in year one to 8.6 ± 0.4 µm/yr in year five. Figure 5 shows a graph of the corrosion rate vs. time. The rate is dropping , but has not flattened out into a consistent rate. The extrapolated long-term corrosion rate suggests a rate of 6 – 7 µm/yr which will need to be verified by the long-term results.

Table 2: Mass loss data and corrosion rates ± one standard deviation

No.	**Exposure Period (hours)**	**Initial Mass (g)**	**Final Mass (g)**	**Mass Loss (g)**	**Corrosion Rate (☞m/yr)**	**Mean Corrosion Rate (☞m/yr)**
01	8684	702.15	698.65*	3.50	13.94	14.5 ± 0.5
11		696.08	692.22*	3.86	15.48	
21		684.77	681.26*	3.51	13.96	
31		715.69	712.33*	3.36	13.34	
02	17.107	701.15	695.46*	5.69	11.74	12.3 ± 0.3
12		711.26	704.92*	6.34	12.78	
22		708.67	702.59*	6.08	12.24	
32		705.21	698.99*	6.22	12.53	
03	25,485	697.38	690.60**	6.78	9.13	9.5 ± 0.8
13		676.70	668.24**	8.46	11.46	
23		697.79	691.59**	6.20	8.37	
33		709.36	702.60**	6.76	9.17	
04	34,578	702.56	692.55**	10.01	9.97	10.0 ± 0.4
14		701.06	691.88**	9.18	9.12	
24		720.36	710.44**	9.92	10.06	
34		680.62	669.88**	10.74	10.75	
05	43,603	688.42	678.44†	9.98	7.88	8.6 ± 0.4
15		693.37	683.00†	10.37	8.20	
25		675.86	664.94†	10.92	8.63	
35		699.76	687.75†	12.01	9.52	

* Stewart, Sergeant, Unglik, 1998
** Sergeant, Stewart, 2001
† Stewart, Unglik, 2002

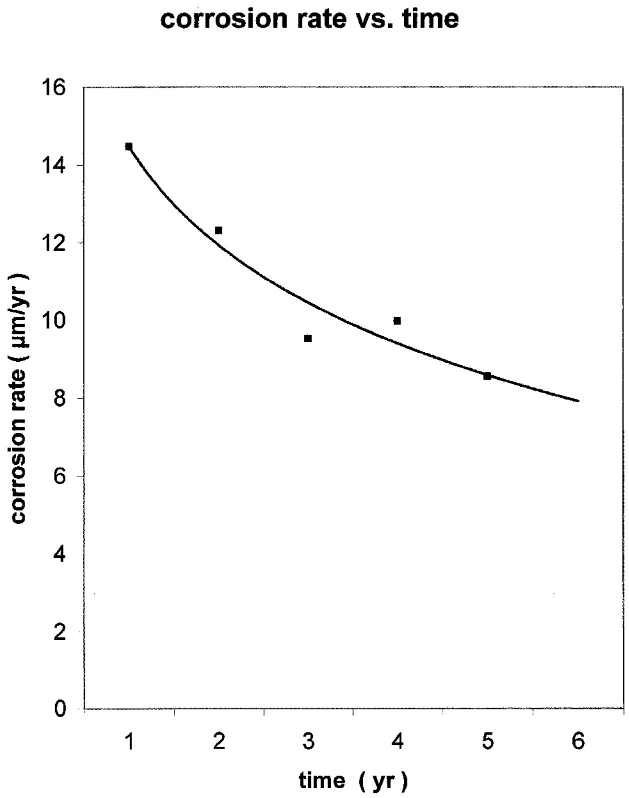

Figure 5: Graph of corrosion rate vs. time

4. Discussion

In his compilation of atmospheric corrosion rates for carbon steel, Einar Mattsson reported rates in rural areas of 4 to 65 µm/yr and in marine environments of 26 to 104 µm/yr. (Mattson, 1982) In comparison, the rate of 8 µm/yr for grey cast iron at Prince of Wales' Fort is relatively low, confirming the anecdotal observations made of the cannon. This was anticipated since the cannon were in fair condition considering they have been at the Fort for almost 250 years and grey cast iron is known to have a low corrosion rate. The environment around Prince of Wales' Fort has low chloride ion concentration, low sulphate ion concentration, and low temperatures combining to produce atmospheric corrosion rates in the range of those typically found in rural, non-marine sites. Extrapolation of the short-term data suggests a long-term corrosion rate of 6 –7 µm/yr. The experiment will continue for another 22 years to confirm the long-term rate.

It is a luxury to follow an atmospheric corrosion test instead of a program of accelerated testing. The atmospheric testing removed the need to precisely determine the environment at Prince of Wales' Fort and reproduce it at elevated temperatures in a laboratory chamber. The coupons are exposed to the same conditions as the cannon. On a microscopic scale, the metal ions and corrosion contaminants are able to react and migrate at a natural speed.

Now that there are short-term results and a long-term study underway, there is the question of how low a corrosion rate is low enough? Is conservation intervention required? For example, extrapolating the corrosion rate to 7 μm/yr predicts the cannon could lose 3 – 4 mm from their surfaces in 500 years. The cannon will still be in place half a millennium from now, but will their markings have survived? The royal cyphers, proof marks, and weight marks are only about 3 to 5 mm thick. In 300 years they will be difficult to read, in 500 years they will be gone. If that information is lost, all that will be left will be basic tubes of cast iron. Bare tubes of metal are not sufficient to convey the significance of the Fort. Although the corrosion rate of the cannon at Prince of Wales' Fort is very slow, it is still enough to endanger the existence of a cultural resource worth preserving and commemorating.

5. Conclusions

The short-term rate of corrosion of grey cast iron at Prince of Wales' Fort was a relatively slow 8.56 μm/yr after five years. This quantitative data can be used for decision-making meetings with the Prince of Wales' Fort staff and other cultural resource professionals working at the Fort. It can communicate the rate of deterioration in a very concrete form: in 500 years the markings will be obliterated All of the people involved in the care and interpretation of Prince of Wale's Fort can now make more enlightened decisions on future preservation regimes for the cannon.

The results would suggest that conservation treatments are required to maintain the historical significance of the cannon at Prince of Wales' Fort. Monitoring the long-term study and determining the best conservation intervention and maintenance regimes for the artefacts at this remote site pose further challenges.

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