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Corrosion of Civil War Era *Sub Marine Explorer*—Part 2

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This is Part 2 of a two-part series on the Sub Marine Explorer. *Part 1 was published in the* September 2010 *issue of* MP. *This article focuses on the experimental results obtained from the corrosion assessment of the American Civil War-era craft's hull.*

The *Sub Marine Explorer* was designed and built by Julius H. Kroehl, who was born in Prussia in 1820. After migrating to the United States in 1838 and becoming a citizen, he served in the Union Navy (United States Navy during the Civil War) as an underwater demolitions expert. He left the Navy in 1863 and began designing a "sub-marine" that would facilitate Union forces' mine removal and obstruction clearance. At the end of the Civil War, he became an engineer for the Pacific Pearl Co., an organization interested in using the craft to recover pearls from deep sea oyster beds in the Bay of Panama. Decompression sickness (the bends), unknown at the time, began to affect the crew in 1869, which led to the abandonment of *Explorer* in the tidal zone of St. Elmo's Island (Isla San Telmo) in the Archipielago de las Perlas, Panama.

The original structural features of *Sub Marine Explorer,* discussed in Part I, have been compromised from over 140 years of exposure in the tidal zone. Drawings by John W. McKay (Figure 1) illustrate major hull damage, on both the port and starboard sides, to the wrought iron above the hull midline and cast iron below it.

Experimental Procedure and Results

Corrosion Potential Measurements

As part of the initial analysis, corrosion potential measurements were taken on the exterior hull and in the interior working chamber. A pneumatic drill and flat mill bit were used to remove oxide and concretion to base metal on both sides of the hull above the midline. After swaging a copper ground wire into a hole drilled through the shell plate, the contact area was sealed with waterproof epoxy. A silver-silver chloride (Ag/AgCl) seawater

equivalent, GMC Electrical† reference electrode (+245 mV conversion to hydrogen electrode) was positioned on transects by a diver directed via hard-wire communication from shore. The corrosion potential, E_{corr}, data were recorded with an HD-160B Wavetech† high-resistance voltmeter. The probe was returned to GMC Electrical after the field operation for calibration verification and was found to have remained within tolerance.

External Hull Horizontal Transects

Six duplicate horizontal transects were obtained from the starboard side and five single transects from the port side. A typical transect is shown in Figure 2.

The corrosion potential, E_{corr}, which is representative of corrosion rate, decreases from bow to stern, as is expected based on previous analysis.[1] The same trend shown in Figure 2 appears seaside (port), although E_{corr} is generally higher than either transect on the starboard side.

External Hull Vertical Transect

All transects were taken horizontally. To determine the effect of tide depth, however, the data were transposed to the vertical. Five vertical starboard transects and five port were calculated at horizontal positions from bow to stern. With one exception, all transects indicate E_{corr} decreases from the hull top to the sand line.

### Interior Working Chamber

Four transects were obtained inside the working chamber on the top centerline, port, starboard, and bottom. Because of heavy concretion, E_{corr} values were generally lower by 20 to 30 mV, indicating lower corrosion rates. All transects in the working chamber consistently show increasing E_{corr} from bow to stern, the reversal reflecting water flow from bow to stern inside the working chamber.

†Trade name.

FIGURE 1
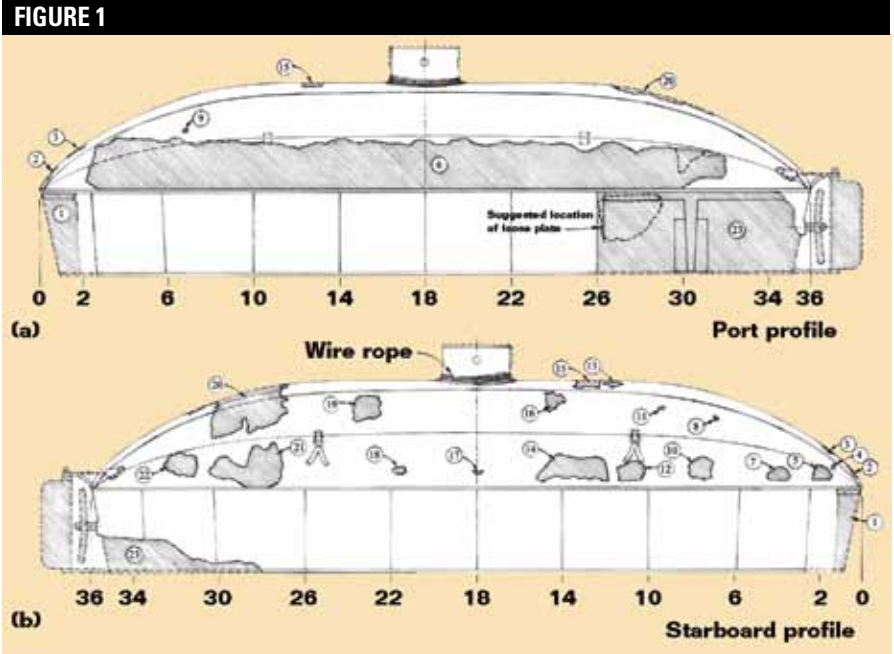
Sub Marine Explorer (1865) external hull damage depicted as of February 2008. (a) Port side and (b) starboard side. Drawings by John W. McKay, March 2008.

FIGURE 2
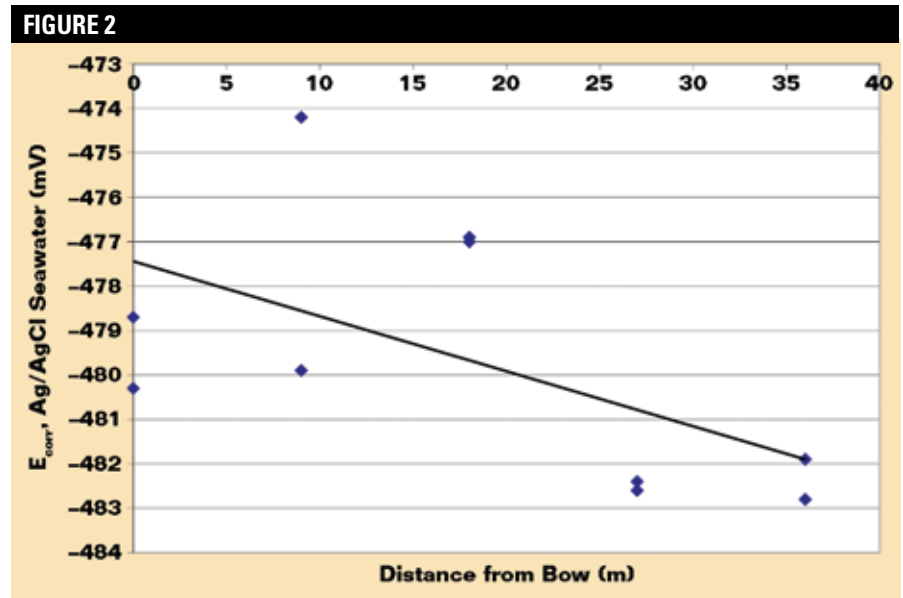
E_{corr} (mV, Ag/AgCl seawater equivalent) transect 20.1/22.2 starboard, horizontal sand line as a function of distance from bow section "0m," cast iron (E_{corr} = –0.124x – 477.4, R^2 = 0.323).

Environmental Monitoring

A YSI 6-series Sonde† sensor was installed at interior and exterior positions to continuously monitor pH, temperature, salinity, and dissolved oxygen (DO) in the water. Data were obtained over a four-day period. The maximum recorded pH was 8.3 and the minimum was 8.1. With two exceptions, DO was tracked high to low tide with a recorded maximum of 9.1 mg/L and minimum 6.6 mg/L for an average of 7.7 mg/L. The highest temperature recorded was 22.2 °C and the lowest was 18.8 °C for an average of 20.5 °C.

TABLE 1
Concretion sample location, properties, and corrosion rate

Sample	Location (Metal)	ρ (g/cm³)	d (cm)	Fe wt%	CECR (mpy)	Comments
06-002	Low stern (cast)	2.24	0.98	57.59	0.8	CECR, exterior, broken, $FeCO_3$
06-003	Midship (wrought)	2.28	1.75	60.98	1.4	CECR, interior, chiseled, 0.1 wt% Ca
06-005	Aft, tower (wrought)	2.30	0.80	48.01	0.5	CECR, interior, drill/saw, 4.3 wt% Ca
06-006	Aft (cast)	2.40	2.36	53.7	1.8	CECR, exterior, drill/saw, 0.3 wt% Ca
06-007	Midship (wrought)	—	—	—	1.8	Calipers, base metal
06-018	Midship (wrought)	3.01	0.95	48.94	0.8	CECR, interior, chiseled 16 wt% Ca
Average					1.2	0.03 mmpy

ρ = concretion density (ASTM D792-00), d = thickness, Fe wt% = iron content, and CECR = concretion equivalent corrosion rate.

Direct Hull Thickness Measurement

An area of the hull adjacent to the ground connection was chosen to measure metal thickness. Shiny base metal appeared after removing 42 mm (1.65 in) of scale from the exterior side. Using a hole drilled through the hull, caliper readings were made and averaged to yield a metal thickness of 12.2 mm (0.48 in). Assuming the hole was drilled in an overlap area, one-half of the original wall thickness remains, which corresponds to an average corrosion rate of 12.2/137 = 0.089 mmpy (3.5 mpy) or 0.044 mmpy (1.8 mpy) per side. This corrosion rate is somewhat higher than the reported 0.036 mmpy (1.4 mpy) for exposure in the tidal zone but lower than that reported for continuous immersion as noted in Part 1.[2]

Sample Collection and Data Acquisition

X-ray diffraction scans of concretion samples revealed magnetite (Fe_3O_4), maghemite (α-Fe_2O_3), and siderite ($FeCO_3$) as major constituents. Unlike concretion samples from the USS *Arizona*, aragonite ($CaCO_3$) was not detected. The x-ray intensity of siderite was relatively low compared to USS *Arizona* concretion because of dilution of the concretion with oxide corrosion products and lower calcium content. Iron exchange with calcium in $CaCO_3$ was consequently low. Maghemite is slightly magnetic.

Concretion Equivalent Corrosion Rate

The first two columns in Table 1 identify sample number, location, and metal type. The third column tabulates density using the submergence method described in ASTM D792-00.[3] Concretion thickness, iron content, and corrosion rate are tabulated in subsequent columns. Equation (1) was used to determine corrosion rates with the exception of Sample 06-007 as noted in the comments column:

$$i_{corr} = 0.8\ \rho d(wt\%Fe)/t\ \text{mpy} \quad (1)$$

where ρ = concretion density (gm/cm³), d = concretion thickness (cm), wt%Fe = wt% of iron (dry basis), and t = exposure time (years).

Concretion samples on the *Explorer* are not totally remnants of marine organisms as is typically the case in quiet seawater, but include imbedded oxide products as previously mentioned.

Available Oxygen Corrosion Rate

As a diagnostic tool to provide information regarding rate control, the apparent oxygen corrosion rate, i_{aocr}, is calculated from Fick's First Law according to Equation (2):

$$i_{aocr} = K\ nFC(O_2)D(O_2)/d\ \text{(mpy)} \quad (2)$$

where K = 5550 (conversion constant), n = number of equivalents per gram atomic weight, F = Faraday constant (96,500 A-s/equivalent), $C(O_2)$ = oxygen concentration (mg/L), $D(O_2)$ = oxygen diffusion coefficient (cm²/s), and d = diffusion thickness (cm).

Using $D(O_2) = 2.24 \times 10^{-5}$, $C(O_2) = 7.7$, and d(ave) = 1.37, collecting terms and constants, Equation (2) simplifies to:

$$i_{aocr} = 5550\ [(2.24 \times 10^{-5})\ 7.7/1.36 \approx 0.7\ \text{mpy}\ (0.0178\ \text{mmpy}) \quad (3)$$

The i_{corr} is substantially higher than i_{aocr} by the ratio $i_{corr}/i_{aocr} = 1.2/0.7 = 1.7$, indicating that cathodic hydrogen discharge supports the corrosion process.[4] Assuming the corrosion rate of completely submerged wrought iron is 70% higher,[1] the ratio increases to $(1.2 \times 0.7 + 1.2)/0.7 \approx 2.86$. This ratio (actual corrosion rate/corrosion rate controlled by oxygen consumption) is defined as the Weins Number, Wn.[4]

Discussion

Because the port side (seaside) undergoes more intermittent splash than the starboard side, high corrosion rates are primarily responsible for the disappearance of hull metal on that side. Mechanical impact from wave-borne floating debris and abrasion are contributing factors. The carryover appears similar to

flash corrosion wherein high oxygen levels yield ferric oxyhydroxide [FeO(OH)]. This corrosion product tends to dry out to form hematite and magnetic maghemite, the reddish-orange to red ferric oxides. Evidence of these oxides was observed in various forms depending upon the degree of dryness on the upper starboard hull.

Conclusions

The reported results are consistent with U.S. Navy corrosion data. The upper limit to the deterioration rate of *Sub Marine Explorer* is unknown because of the extent of mechanical impact and abrasion. As discussed, the corrosion rate is variable depending upon protection against corrosion that is provided by concretion and the position of various parts of the hull in relation to tide flow pattern and flash corrosion from carryover.

An average corrosion rate of 0.03 mmpy (1.2 mpy) is estimated for the exterior hull side. Assuming the same corrosion rate on the interior hull side, the average corrosion rate for both sides is nearly 0.061 mmpy (2.4 mpy). Based on data and observations on the upper starboard side, about one-half of the original thickness of the upper outer hull remains; structural integrity of this part of the hull structure is reaching critical stage. Corrosion rate control involves the interaction of oxygen consumption and hydrogen discharge with the latter apparently being dominant.

The authors recommend that cast and wrought-iron samples be obtained from the site for detailed metallographic examination to: 1) confirm the assumption that the cast portion of *Explorer* is gray cast iron in terms of today's classification, and 2) determine corrosion rate from the depth of the graphitized zone in the cast iron microstructure for comparison with results in Table 1.

Acknowledgments

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Editor's note: Sub Marine Explorer *was recently featured in the Smithsonian Network's "America's Lost Submarine" and Speigel TV International's "The Search for Explorer," History U.K. and U.S. versions.*

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