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Corrosion of Civil War Era *Sub Marine Explorer*—Part 1

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Sub Marine Explorer, built near the end of the American Civil War and later abandoned in the Bay of Panama tidal zone, is one of the first submarines designed with ballast compensation. This article includes a short history of the craft, its present condition, literature review, and the methodology used to assess corrosion. Experimental results will be presented in Part 2 next month.

The *Sub Marine Explorer* is one of five submersibles (submarines) constructed prior to 1870 that have survived either in museums or as in situ archaeological sites around the world. Since 1869, the wreck of *Explorer* has emerged at low tide on the beach of Isla San Telmo, Archipiélago de las Perlas, Panama, located ~75 km southwest of Panama City in the Bay of Panama. In 2001, James Delgado visited the site. Locals described the wreck as a World War II-era Japanese midget submarine. Delgado consulted with Richard Wills, an expert on American Civil War submarines, and confirmed that the well-preserved wreck was the *Sub Marine Explorer* from the Civil War period.¹

Historical Background

Julius H. Kroehl was the designer of the *Sub Marine Explorer*. He was born in Prussia in 1820 and came to the United States in 1838. In addition to iron fabrication, his interests were diving and underwater explosives. Following assignments in the Union Navy (United States Navy during the Civil War), he designed a “submarine” that would facilitate the Union forces’ mine removal and obstruction clearance. Kroehl’s craft included a pressurized air storage chamber that allowed the pressure of the working chamber to be equalized with the ambient pressure prior to diving. With internal air pressure preventing the sea from flooding the working chamber, workers could access the seafloor or divers could exit and re-enter the submarine through keel hatches to disarm mines, set charges, or perform other duties. This was one of the first successful uses of a “lock-out” capability for a submarine.²

Kroehl became chief engineer of the Pacific Pearl Co., an organization interested in recovering pearls and shells from deep sea oyster beds in the Bay of Panama Las Perlas Islands archipelago. He

FIGURE 1



Sub Marine Explorer, St. Elmo's Island, Bay of Panama, February 2006. Donald Johnson photograph.

began constructing the submarine in Brooklyn, New York in 1864. Kroehl completed construction in November 1865 and named his craft *Sub Marine Explorer* and tested it through May 1866.

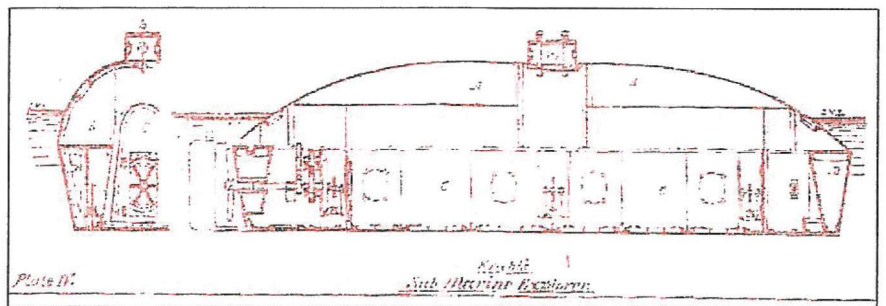
In November 1866, the submarine was partially dismantled and shipped to the Caribbean side of Panama, then transported by rail across the isthmus to the Pacific coast. After reassembling and testing, Kroehl died of fever in September 1867. A new engineer, Henry Dingee, had the craft towed to the archipelago, where it was used to harvest pearls in August 1869. The submarine was then abandoned and its activities ended because the crew was incapacitated, likely as a result of the bends or decompression sickness.

Hull Construction

Explorer is 11-m (36-ft) long, with a maximum external height of 2.4 m (8 ft). The conning tower extends 0.4 m (1.4 ft) above the hull's centerline. The maximum beam is 3 m (10 ft) with tapering at bow and keel. *Explorer's* principal feature is a "working chamber," a 10-m (33-ft) long corridor with a breadth of 1.5 m (5 ft) amidships. The water ballast chamber was located below the working chamber and the compressed air chamber was located above the working chamber. Aside from the conning tower, the only other access points were two manholes and two hatches in the hull bottom that were used when the workers and divers collected oysters.¹ A single, four-blade propeller mounted inside the rudder was manually operated by a hand crank. Figure 1 shows a starboard view of the submarine taken from the shore. Figure 2 is a 1902 drawing of the submarine based on the 1865 plans.

The hull is divided longitudinally into two sections joined at the 1.2-m (4-ft) line. The lower hull, a complex series of iron castings, weighed 25,900 kg (57,100 lb).

FIGURE 2



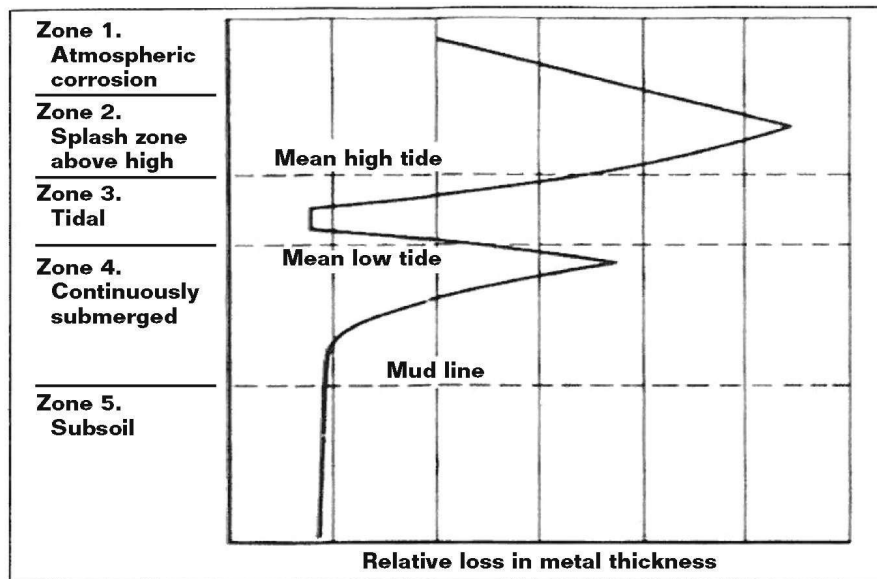
Sub Marine Explorer (1902) as redrawn by Baird. Julius H. Kroehl, designer.²

The wrought iron upper hull weighed 14,090 kg (31,060 lb), giving an overall design weight of ~44 tons.¹ Kroehl intended for the heavier cast iron to stabilize the craft with seawater ballast for submerging. The keel is cast iron plate, 44.5-mm (1 3/4-in) thick, and is now open to the freely flowing tide.

Five overlapping, double-riveted countersunk 12.7-mm (1/2-in) wrought iron strakes form the upper hull.¹ The upper and lower shells overlap 100 mm (4 in). Total thickness of the upper hull is

assumed to be 25.4 mm (1 in), based on historical records. Two hundred eighty five 25.4-mm diameter rods, assumed to be wrought, tie the upper hull strakes to the top of the ballast and working chambers. A field survey conducted in 2004 generally confirmed structural information obtained from archival records. Access to the lower hull was limited because it was buried in sand, rock, and gravel to a depth of ~1 m (3 ft). A second field trip was organized by Delgado in 2006. Johnson and Murphy joined the research team

FIGURE 3



Steel pile corrosion after five years of exposure, Kure Beach, North Carolina. International Nickel Co.⁵

to assess corrosion on site and select samples for laboratory analysis.

Metallurgy

Because the submarine was built before the age of steel, primary structural materials are wrought and cast iron. A typical composition (wt%) of wrought iron is 0.06 C, 0.045 Mn, 0.101 Si, 0.068 P, and 0.009 S, with 1.97 slag. Because the carbon content is low, slag is imbedded in a ferrite (low-temperature iron phase) matrix. Cast iron is an alloy of iron, carbon, and silicon, with a typical composition (wt%) of 2.7-3.6 C and 1.0-3.0 Si. The carbon content is too high to dissolve completely in solid iron; hence, the excess appears as graphite flakes imbedded in a pearlite matrix. Pearlite, a mixture of ferrite and iron carbide (Fe_3C), is clearly identified by its layered microstructure. Cast iron manufacture has a long history, but it wasn't until the mid-19th century (1880) that furnace capacity increased from ~6 to 100 tons/day. Manufacture of the 30 tons of cast iron used for *Explorer* probably required several heats, causing less uniformity than today's production methods.³ Steel chemistry is quite different.⁴

Corrosion

Background

In the late 1970s, the U.S. Navy conducted comparative corrosion studies of steel and wrought iron exposed at mean low tide in the Pacific Ocean off the Panama Canal and continuously submerged in seawater at Cristobal, Panama Canal Zone. After exposure at mean low tide for 16 years, the average corrosion rate of steel, calculated from weight loss, was 0.069 mmpy (2.7 mpy). After continuous immersion for 16 years, the average corrosion rate of steel remained the same at 0.069 mmpy. After exposure at mean tide for eight years, the average corrosion rate of wrought iron was 0.036 mmpy (1.4 mpy). After eight years of continuous immersion, the average corrosion rate of wrought iron increased by more than 70% to 0.061 mmpy (2.4 mpy).⁵⁻⁶

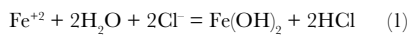
Comparative corrosion rates of wrought and cast iron are highly variable depending on the duration and type of seawater exposure, the extent of electrical continuity, and the ratio of anode to cathode area.⁶⁻⁷

Visual Examination and Products

Observations were organized around a portion of the tide cycle illustrated for steel in Figure 3.⁵ It was assumed that relative changes from zone to zone are similar for wrought and cast iron. Corrosion of iron-based alloys in the tidal zone is complex because of continuous changes in the environment. Starting with the atmosphere above high tide (Zone 1, Figure 3), corrosion rate is relatively low and increases into the splash area (Zone 2), which is defined as the region just above high tide. Although *Explorer* is completely submerged at high tide, wave-splash carryover of corrosion products from port to starboard continues as the tide rises and falls.

The outer hull corrosion product is likely ferric oxyhydride [$\text{FeO}(\text{OH})$], which is orange-brown in color. In most applications, the oxyhydrides convert to hematite, alpha Fe_2O_3 , and maghemite, gamma Fe_2O_3 , both of which are reddish brown, with the latter being slightly magnetic.⁸ Carryover has diminished with time because of the severe loss of upper hull wrought iron. The extent of metal loss caused by erosion and debris impact as compared to corrosion is unknown, although accumulated onshore logs and debris suggest that major impacts have occurred. In addition, abrasion, wave action, and splash occasionally interrupt the formation of concretion (hard marine biofouling). While ~15% of the cast iron hull below the craft's 4-ft (1.2-m) line is destroyed, more wrought iron has been destroyed above this line, including a major portion of the port side (seaside) and numerous areas starboard aft of the centerline. Oxide scale is dominant starboard, partly from accumulated carry over. Oxide scale is cathodic to base metal, and it may contribute to galvanic corrosion in this area. Barnacles and associated marine organisms can live in and out of water, feeding during the submerged periods; hence, concretion

continues to accumulate regardless of the tide level. A black, greasy substance on external hull areas could be either magnetite promoted by limited oxygen at the oxide corrosion product-metal interface, or iron sulfide (FeS), which gives evidence of sulfate-reducing bacteria (SRB) activity.⁵ Beneath concretion or accumulated oxide, deaeration promotes the diffusion of chloride ions into the concretion/metal interface. Ferrous ions hydrolyze and form iron hydroxide and hydrogen chloride (HCl), which cause a decrease in pH (Equation [1]). Hydrogen ion discharge then supports corrosion in addition to oxygen consumption.⁹



As conditions became anaerobic, magnetite or FeS, as a soft adherent layer, allowed the concretion to part easily from the hull due to abrasion and impact. Although the interior is subject to a tidal rush of seawater, concretion remains stable inside the working compartment. Contact between the lower hull, rock, and coarse sand creates oxygen cell corrosion because the hull is continuously submerged and abraded in that area. On a much larger scale, galvanic corrosion from electrical continuity between cast iron and wrought iron is a contributing factor. Over time, the area ratio of cast to wrought has increased.

Biological Factors

The first organisms to attach include diatoms, filamentous algae, barnacles, and larvae of other marine animals. Data indicate that the corrosion rate decreases as concretion thickness increases and oxygen availability decreases.¹⁰⁻¹¹ After concretion buildup, the corrosion rate increases to a steady state as SRB accelerate cathodic discharge of hydrogen ions to hydrogen. Without hydrogen ion discharge, the corrosion rate would remain low because of limited oxygen availability.¹²

Concretion Equivalent Corrosion Rate

Concretion equivalent corrosion rate (CECR), a nondestructive method to estimate the corrosion rate of iron-based alloys in seawater, was applied to *Sub Marine Explorer* and will be discussed in Part 2. Equation (2), also applied to two WWII Japanese midget submarines,¹⁵⁻¹⁶ is given by

$$i_{\text{cccr}} = k\rho d(\text{wt}\% \text{ Fe})/t \quad (2)$$

where i_{corr} is the corrosion rate determined by CECR, $K = 0.020$ for i_{corr} in mmpy, $K = 0.8$ for i_{corr} in mpy, ρ is the concretion density (gr/cm^3), $\text{wt}\% \text{ Fe}$ is weight percent iron (dry basis), d is concretion thickness (cm), and t is exposure time.

Conclusions

Corrosion in the tidal zone is complex and variable, subject to weather patterns, alternate wetting and drying, splash carryover, and mechanical impact. A correction factor of 1.6, developed from metal coupon data on the USS *Arizona*, has been incorporated to account for iron lost prior to the surface being covered with concretion. Part 2 (October 2010 *MP*) will cover corrosion measurements, tests, and results.

Acknowledgments

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International Omaha Section for providing undergraduate scholarship funding for student laboratory assistance at the University of Nebraska-Lincoln and support of the National Park Service Submerged Resources Center. Archaeological survey team members in 2006 were James Delgado, Todd Croteau, Bert Ho, Michael McCarthy, Larry Murphy, Joshua Price, Don Johnson, and Karl Vandenhole.

References

- 1 J.P. Delgado, "Archaeological Reconnaissance of the 1865 America-Built *Sub Marine Explorer* at Isla San Telmo, Archipiélago de las Perlas, Panama," *The Intl. J. of Nautical Archaeology* 35, 2 (2006): pp. 230-252.
- 2 The Pacific Pearl Co., Inc. under the Laws of New York, E.S. Dodge & Co., Printer, 84 John St., NY, 1865.
- 3 *The Making, Shaping and Treating of Steel*, United States Steel Corp., 1957.
- 4 *Metals Handbook*, Vol. 10, 9th ed. (Metals Park, OH: ASM, 1979), p. 510.
- 5 M. Schumacher, ed., *Seawater Corrosion Handbook*, (Park Ridge, NJ: Noyes Data Corp., 1979), pp. 367-387.
- 6 *Metals Handbook*, Vol. 13, Corrosion, 9th ed. (Metals Park, OH: ASM, 1979), p. 83.
- 7 I.D. McCleod, C.V. Ruppe, J.F. Barstad, eds., "In Situ Corrosion Measurements and Management of Shipwreck Sites," *Intl. Handbook of Underwater Archeology*, pp. 697-714.
- 8 C.P. Dillon, "Corrosion Basics: Iron and Steel," *MP* 45, 8 (2006): p. 68.
- 9 D.A. Jones, *Principles and Prevention of Corrosion* (Upper Saddle River, NJ: Prentice-Hall, Inc., 1993), pp. 212 and 53.
- 10 J.D. Makinson, D.L. Johnson, M.A. Russell, D.L. Conlin, L.E. Murphy, "In Situ Corrosion Studies on the Battleship USS *Arizona*," *MP* 41, 10 (2002): pp. 56-60.
- 11 D.L. Johnson, B.M. Wilson, J.D. Carr, M.A. Russell, L.E. Murphy, D.L. Conlin, "Corrosion of Steel Shipwrecks in the Marine Environment: USS *Arizona*—Part I," *MP* 45, 10 (2006): pp. 40-44.

- 12 J.C. Kotz, K.F. Purcell, *Chemistry and Chemical Reactivity* (Philadelphia, PA: Saunders College Publishing, 1987), pp. 773-736.
- 13 D.L. Johnson, B.M. Wilson, J.D. Carr, M.A. Russell, L.E. Murphy, D.L. Conlin, "Corrosion of Steel Shipwrecks in the Marine Environment—Part II," *MP* 45, 11 (2006): pp. 54-57.
- 14 M.A. Russell, D.L. Conlin, L.E. Murphy, D.L. Johnson, B.M. Wilson, J.D. Carr, "A Minimum-Impact Method for Measuring Corrosion Rate of Steel-Hulled Shipwrecks in Seawater," *IJNA* 35.2 (2006), pp. 310-318.
- 15 B.M. Wilson, D.L. Johnson, H. Van Tilburg, M.A. Russell, L.E. Murphy, J.D. Carr, R.J. De Angelis, D.L. Conlin, "Review of Corrosion Studies on USS *Arizona* with Application to WWII Japanese Midget Submarine," accepted for publication in the *JOM*, TMS, October 2007.

- 16 Unpublished Report, D.L. Johnson, J.D. Carr, "Corrosion Analysis—Three Piece Japanese Midget Submarine," NOAA, Pacific Islands Region and Submerged Resources Center, NPS, August 8, 2009.

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

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