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2007

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The assessment of corrosion on the USS Arizona *included the pioneering development of a minimum-impact cost-effective technique to determine the corrosion rate of steel-hulled shipwrecks in seawater. The technique, with potential application worldwide, is illustrated in this paper with the application to a World War II Japanese midget submarine submerged in deep waters off the Oahu, Hawaii, coast.*

INTRODUCTION

In the early morning hours of December 7, 1941, five Japanese class I fleet submarines launched five midget submarines ten miles off Pearl Harbor. The mission was to covertly slip into the harbor, wait until the attack by Japanese forces on Pearl Harbor began, then fire their torpedoes. Each vessel was 23.7 m long, had a beam of 1.8 m, and a 1.4 m conning tower. Each submarine carried a crew of two and two torpedoes. At 3:57 a.m., Ensign R.C. McCloy, minesweeper *Condor's* officer of the deck, spotted something off his port bow and called over Quartermaster R.C. Uttrick. "That's a periscope sir, and there aren't meant to be any subs in this area." Ensign McCloy blinked a semaphore to USS *Ward*, "Sighted submerged submarine.

. . ." Captain William W. Outerbridge, who earned his command only two days before, sounded general quarters, but secured at 4:35 a.m. having made no contact. At 5:50 a.m., *Antares'* skipper, Commander Lawrence C. Grannis, reported another sighting to *Ward*. By 6:40 a.m., Captain Outerbridge spotted a conning tower trailing *Antares* at the entrance to Pearl Harbor, closed to 45.7 m, and fired a 10.2 cm round into the target. Although surviving documentation does not reveal that the site was the submarine sunk by *Ward*, evidence from the site, such as a shell hole at the starboard base of the conning tower (Figure 1) corresponds to the action report filed by *Ward* identifying the submarine as the first vessel sunk by the U.S. Navy in the Pacific war of World War II.[1] The #3, 10.2 cm gun from *Ward*, which fired the shot that sank the submarine, is now located on the Capitol Mall in St. Paul, Minnesota (Figure 2).

At 7:53 a.m., the Japanese initiated a surprise air attack against U.S. Forces stationed at Pearl Harbor and other military sites on Oahu, Hawaii. During the first wave, consisting of 183 fighters and torpedo bombers, *Arizona* became a total loss when a bomb penetrated the deck and sympathetically detonated its forward magazine. After the second wave of the attack consisting of 167 aircraft was over, 22 additional ships were damaged or totally lost with 2,403 killed in action, 1,173 of whom were lost on *Arizona*.

In August 2002, researchers in a Hawaiian Undersea Research Laboratory (HURL) submersible discovered this Japanese midget submarine approximately 4.83 km offshore from the entrance to Pearl Harbor, in 406.7 m of

Figure 1. A shell hole at the starboard base of the conning tower on the Japanese midget submarine. Photo courtesy of the National Oceanic and Atmospheric Administration/Hawaiian Undersea Research Laboratory.

Figure 2. A number 3 gun, USS *Ward*, standing in front of the Minnesota Capitol, St. Paul, Minnesota. Robert Hall photo.

water. In a later submersible descent, several small segments of marine concretion were recovered from the aft end of the midget sub by the robotic arm of HURL's *Pisces* submersible (Figure 3). These samples were analyzed in metallurgical and chemistry laboratories at the University of Nebraska–Lincoln, and x-ray diffraction measurements were conducted at the Air Force Research Laboratory, Eglin Air Force Base, Florida. The purpose of this paper is to review Corrosion Equivalent Corrosion Rate (CECR) methodology,[2] a minimum impact technique pioneered on *Arizona*, and its application to estimate the average corrosion rate of the external hull of the midget submarine. A second purpose is to present the results of x-ray diffraction studies on the concretion samples and to relate these results to physical and chemical properties of the submarine's concretion.

TEST SITES

USS *Arizona*

The *Arizona* remains submerged where it was sunk by Japanese forces on December 7, 1941. An estimated 1.9 million liters of fuel oil remain aboard, either in original bunkers or trapped beneath overheads of numerous undamaged compartments. Limited salvage operations on the vessel were terminated in 1942. A thorough archeological documentation of the wreck was initiated by the National Park Service and the U.S. Navy at the request of the USS *Arizona* Memorial superintendent in 1983. A detailed document including history, drawings, photographs, analysis,

and recommendations for site management was published in 1990.[3] This initial document reported the earliest attempt to examine in-situ corrosion processes on a sunken steel ship. An interdisciplinary research program, the USS *Arizona* Preservation Project, began in 1999 to conduct a comprehensive study of corrosion, structural integrity, microbiology, sub-surface geology, and oceanography relevant to the in-situ site formation processes affecting the vessel. The data are providing critical inputs to a finite element model, which will constitute a composite research product to be used by managers in making future preservation decisions about the ship.

Several documents have been published since the Preservation Project's inception. The following references are specific to corrosion studies on the *Arizona*, and serve as the background for research done on the Japanese midget submarine that is the subject of this paper. References 4–7 contain information

concerning the metallurgy,[4] potential/pH and metal coupon data,[5,6] and minimum impact corrosion rate measurement technique.[2,7]

Japanese Midget Submarine

The midget submarine hull was fabricated from cold-rolled MS44, low-carbon, basic open-hearth steel to an original wall thickness of 8 mm.[8] With no direct access to the submarine's hull, it was impossible to obtain metal samples that could directly reveal the extent of metal loss by laboratory metallographic methods. Ultrasound measurements were not attempted because experience with the heavily concreted *Arizona* hull has not provided conclusive data,[6] and the method has not proven to be reliable with current technology. Electrochemical methods might be useful, but instantaneous data may not accurately reflect long-term corrosion. In addition, it would be expensive to monitor and service in-situ instrumentation on site. As a result, the Japanese midget submarine discovered in 2002 appeared to be a suitable test site for the application of CECR methodology.[2,7]

METAL/CONCRETION INTERACTIONS

USS *Arizona*

$FeCO_3$ (siderite), $CaCO_3$ (aragonite), and Fe_3O_4 (magnetite) were the three major minerals present in *Arizona* concretion identified by a Siemens x-ray diffractometer. Iron contents varied from 18–65 wt.%, with an average of approximately 50 wt.% using environmental scanning-electron microscope (ESEM)

Figure 3. The aft end of the Japanese midget submarine during collection of concretion samples. Photo courtesy of the National Oceanic and Atmospheric Administration/Hawaiian Undersea Research Laboratory.

cross section scanning.[7] Based on these observations, studies were initiated on *Arizona* to correlate iron content in the concretion with the average corrosion rate obtained from analysis of metal coupons removed from the hull in 2002. Results of this correlation are shown in Equation 1, where i_{corr} (CECR) is given. (All equations are shown in the table on page 17.) In this equation, K = 0.020 for i_{corr} in millimeters per year (mmpy); ρ is concretion density (g/cm³); wt.% Fe is weight percent iron; d is concretion thickness (cm); and t = 61 is exposure time (y).

Japanese Midget Submarine

As with *Arizona* concretion, a Siemens x-ray diffractometer was used to scan the cross section of the midget submarine concretion samples from shipside to seaside at distances 0.03 cm, 0.05 cm, 0.08 cm, 0.13 cm, and 0.17 cm for siderite, goethite (FeOOH), and magnetite.[11] The diffractometer was situated on the calculated 2-theta peak for each mineral, and then scanned on either side from 0.5 to 1 degree so as to include the entire profile caused by line broadening. Figures 4, 5, and 6 show the profiles for siderite, goethite, and magnetite, respectively, as a function of 2-theta angle and linear intensity (counts per second, Cps). As a general rule, intensity is approximately proportional to the concentration of a measured compound. Siderite occurs throughout the cross section, but appears to reach maximum concentration at the

interior of the concretion toward seaside at 0.17 cm. Goethite is highest in concentration toward shipside at 0.03 cm, and lowest toward seaside at 0.17 cm. Similarly, magnetite is highest in concentration toward shipside at 0.03–0.05 cm and lowest toward seaside at 0.17 cm. Aragonite does not appear in the x-ray scans of the submarine concretion, although it does appear in *Arizona* concretion as mentioned previously.

Maximum siderite toward seaside (Figure 4) suggests that iron diffusion through the concretion is fast relative to siderite formation kinetics. The exact mechanism by which siderite forms is unknown, but it is probably related to iron exchange with calcium in calcium carbonate.[12] North reported that the original aragonite skeletal material was converted into various iron compounds with siderite being the most common. Maximum goethite and magnetite toward

shipside (Figures 5 and 6, respectively) suggests that oxygen diffusion is fast relative to iron oxide formation kinetics. The presence of goethite in the concretion rather than at the metal/concretion interface, as in the case of *Arizona*, may explain the higher iron content in the midget submarine concretion than in *Arizona* concretion. Although a chloride-containing oxide, akaganeite, appears in *Arizona* scale, no chloride containing oxides appear in the midget submarine concretion. Other research indicates that akaganeite forms after the concretion is exposed to air,[13] which may explain the presence of this mineral in *Arizona* concretion, but it does not explain its absence in the midget submarine concretion.

CORROSION

Concretion Equivalent Corrosion Rate

From a collection of midget submarine concretion samples, the six largest were designated as samples S1, S2, S3, S4, S5, and S6. To begin, concretion density was measured, then thickness and water content were determined. Last, the samples were ground to a fine powder and delivered to the Department of Chemistry analytical laboratory at the University of Nebraska-Lincoln for iron analysis using wet chemical methods. The data, including CECR data from Equation 1, are given in Table I.

The CECR predicts an average corrosion rate of 0.014 mmpy, corresponding to a total hull loss of 0.9 mm, with approximately 7.1 mm of metal remaining. For comparison, *Arizona* concretion contained significantly lower iron, varying between 22–48 wt.%, greater concretion thickness, averaging 1.8 cm,

Table I. Physical and Chemical Properties of Japanese Midget Submarine Concretion, and Calculated Concretion Equivalent Corrosion Rate (CECR)

Sample	Fe (wt.%)	d (cm)	Density* (g/cm³)	H₂O (wt.%)	i_{corr} (CECR)** (mmpy)
S1	52.7	0.335	2.017	25.5	0.012
S2	55.5	0.272	2.511	20.7	0.012
S3	61.8	0.523	1.619	50.3	0.017
S4	63.0	0.424	1.520	54.5	0.013
S5	58.3	0.447	1.809	39.6	0.015
S6	54.7	0.345	2.005	27.8	0.012
Average	57.7	0.39	1.91	36.4	0.014

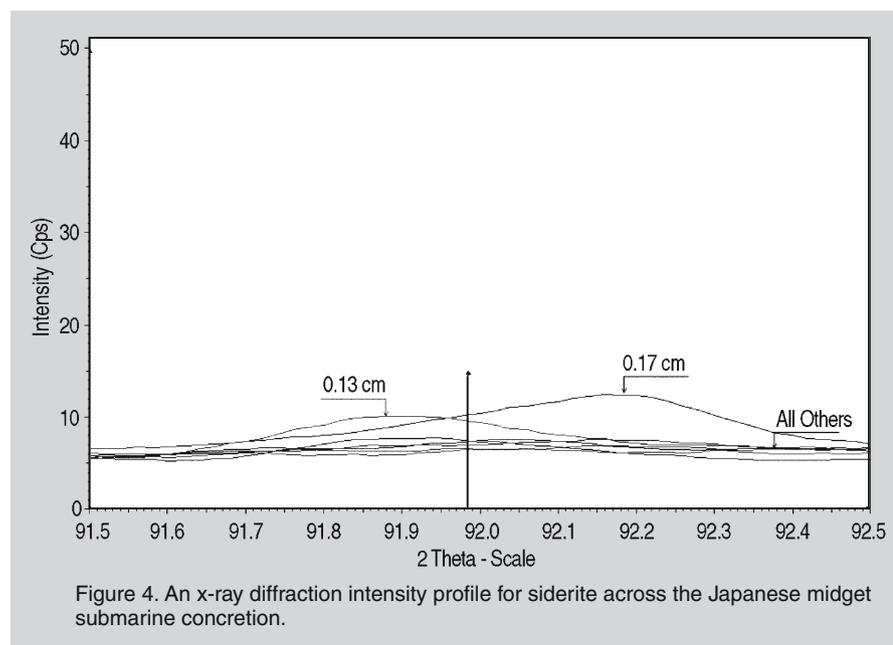* ASTM Designation D792-00
** Equation 1

Figure 4. An x-ray diffraction intensity profile for siderite across the Japanese midget submarine concretion.

greater concretion density, varying from 1.9–2.5 g/cm^3, and lower water retention at approximately 14 wt.%.

Corrosion Mechanism—Limiting Current

In sea water, oxygen reduction at cathodic sites is typically the driving force for the corrosion process. Assuming oxygen reduction is the only cathodic reaction, the limiting corrosion rate is calculated using Fick's First Law according to Equation 2, where: $i_{corr}(l)$ is the limiting corrosion rate (mpy), $J = KDC/d$ is the oxygen flux through concretion (g O_2/cm^2/s), $K = 0.012$ for i_{corr} in mmpy,

Equations

$$i_{corr}(CECR) = \frac{K\rho d(wt.\%Fe)}{t} \qquad (1)$$

$$i_{corr}(O_2 \text{ reduction}) = i_{corr}(l) = \frac{KDC}{d}nF \quad [mmpy] \qquad (2)$$

$$i_{corr}(O_2 \text{ reduction}) = \frac{(0.012)(1.72 \times 10^{-5})(4.42)}{0.39}(0.125)(96,500) \cong 1.1\,mpy \ \ [0.028\,mmpy] \qquad (3)$$

D is the diffusion coefficient for O_2 in water (cm^2/s), d is concretion thickness (cm), n is the number of equivalent electrons transferred per gram atomic

weight, F is the Faraday constant (A·s/e$^-$), and C is the oxygen concentration at the concretion/seaside interface, or gradient across the concretion assuming C at the concretion/metal interface $\cong$ 0 (mg/L).

The diffusion coefficient for oxygen in water, D, is estimated at 8.8°C using $D_{25} \cdot (T/T_{25})(\mu_{25}/\mu)$, where D_{25} is the diffusion coefficient for oxygen at 25°C, μ is the viscosity of water, and T is absolute temperature. At 8.8°C, D equals 1.72×10^{-5} cm^2/s[14] and C(sat) = 47.24%. Based on a mean temperature of 8.8°C at a water depth of 406.7 m, and a mean salinity of 34.1, C(sat) converts to C = 4.42 mg/L, with a standard deviation of 0.9 mg/L.[15] From Table I, d (average) = 0.39 cm, n = 2/16 = 0.125, and F = 96,500 A·s/e$^-$. When these values are substituted into Equation 2, Equation 3 results.

Comparison to the CECR indicates that i_{corr} (O_2 reduction) is greater than i_{corr} (CECR) by approximately 0.014 mmpy. This difference may be caused by rate-limited mineral formation kinetics in the concretion. It is of interest to note that the corrosion rate from coupon measurements on *Arizona* is greater than that calculated from Equation 2, the opposite of that observed on the midget submarine.[6] The authors suggest that hydrogen discharge, stimulated by microbial activity, supports corrosion on *Arizona*, but is less of a factor on the midget submarine.[16]

CONCLUSION

Based on CECR, the average corrosion rate of the Japanese midget submarine hull, submerged in 406.7 m of sea water, is estimated to be 0.014 mmpy, corresponding to a 61 year loss of approximately 11% of its original hull thickness. Iron in the midget submarine concretion appears in the form of the minerals goethite, magnetite, and sider-
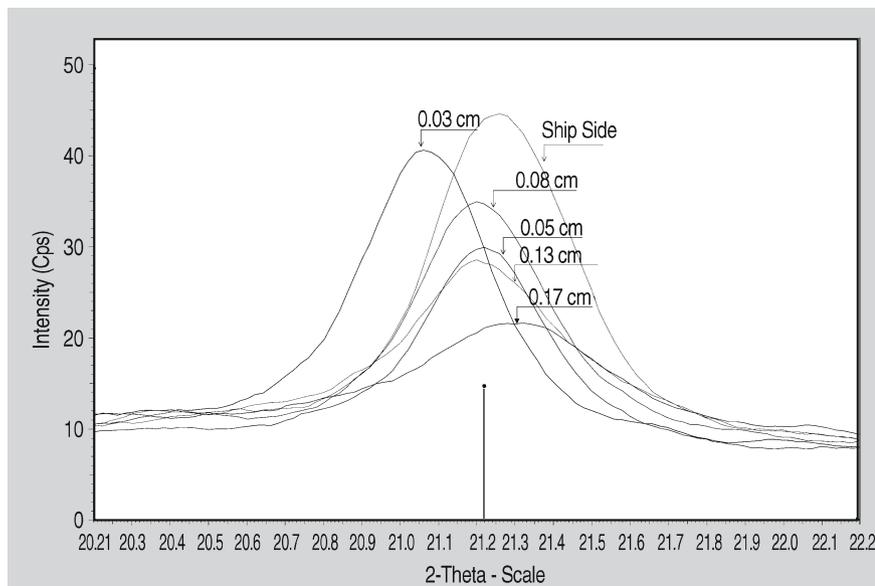

Figure 5. X-ray diffraction intensity profiles for goethite across the Japanese midget submarine concretion.
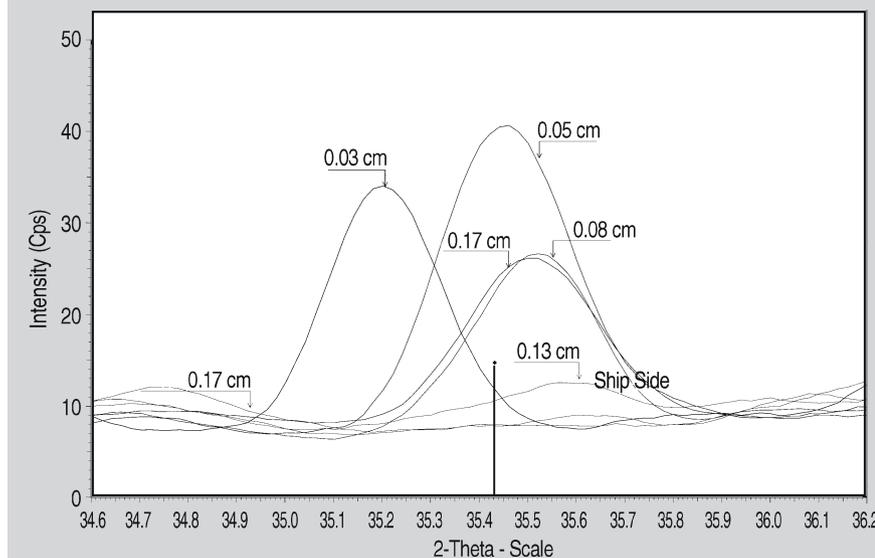

Figure 6. X-ray diffraction intensity profiles for magnetite across the Japanese midget submarine concretion. The double peaks at 0.17 cm result from heterogeneity in the concretion.

ite. Formation kinetics of these minerals may be rate limiting. Unlike *Arizona* concretion, aragonite was not detected. High water retention, combined with low concretion thickness, may explain the high oxygen availability at the metal/concretion interface. To lend support to these conclusions, two avenues of approach are being pursued. The first is to search for other marine sites where it is feasible to collect concretion samples, and measure on-site environmental parameters: oxygen saturation (%), temperature, salinity, and pH. The second approach is to conduct an in-depth study of concretion morphology with corresponding experimental measurement of iron and oxygen diffusivity, and kinetics of formation of iron-bearing minerals in the concretion.

While water depth reflects environmental properties, incorporation of these environmental properties directly into Fick's First Law for limiting current can be used to better understand the corrosion process.

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