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Makinson, John D.; Carr, James D.; Russell, Matthew A.; Conlin, David L.; and Murphy, Larry E., "In Situ Corrosion Studies on the Battleship USS Arizona" (2002). *Mechanical & Materials Engineering Faculty Publications*. 399.
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In Situ Corrosion Studies on the Battleship USS *Arizona*

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U.S. National Park Service Submerged Resources Center archeologists and University of Nebraska-Lincoln metallurgists are assessing hull corrosion by drilling through accumulated concretions and measuring pH and corrosion potentials. Concretion samples are being analyzed to determine the role of microbes in the corrosion process, identify chemical species, and measure electrical and physical properties. The lowest values of pH and E_{corr} occur at the metal/concretion interface. Analysis suggests a variable corrosion rate supported by hydrogen discharge and/or oxygen reduction inside the concretion.

The battleship USS *Arizona* was launched in 1916, modernized between 1929 and 1931, and served in the Western Atlantic and the Eastern and Central Pacific. On December 7, 1941, the ship was sunk while moored alongside Ford Island during the surprise attack by Japanese forces at Pearl Harbor. The hull from the main deck to the keel has been submerged in position since that time at a list to port (left) of ~2.2 degrees. Eleven hundred seventy seven USS *Arizona* crew lost their lives, and more than 900 remain entombed. As a shrine and national memorial, constraints are placed on entry into the interior of the hull, and penetration of the hull fabric requires preauthorization. Fuel oil continues to emerge from the interior at the rate of ~1 L/day. An estimated 500,000 gal (1.9 million L) of fuel oil remain contained in bunkers or trapped in compartments above.

This report is second in a series of articles that will complement the *Arizona*'s structural assessment and recommendations for site management consideration.[1] Based on observations to date, hull collapse is not imminent but hull and interior assessment is timely as deterioration continues.

In 1983, the U.S. National Park Service (NPS) Submerged Resources Center (Santa Fe, New Mexico) was tasked with mapping and photo-documenting the remains of the *Arizona* in its final resting place in Pearl Harbor. The task was later broadened to include an inventory of bio-data and a corrosion assessment. The results of this study were published in 1990.[2] The University of Nebraska-Lincoln (UNL) conducted an analysis of the corrosion data from this report in mid-1998. The article presents the results of this analysis as well as findings from follow-up field operations in September 1999 and September 2000.
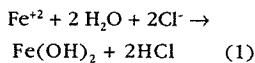
Literature Review

The complexity of the corrosion process on the submerged hull is evident from the NPS report[2] and from initial field operations conducted by NPS and UNL researchers in 1999. Iron is not a biologically toxic metal; when immersed in seawater, it will be colonized by marine organisms. As a result, the formation of hard biofoul or calcareous concretions on the surfaces of
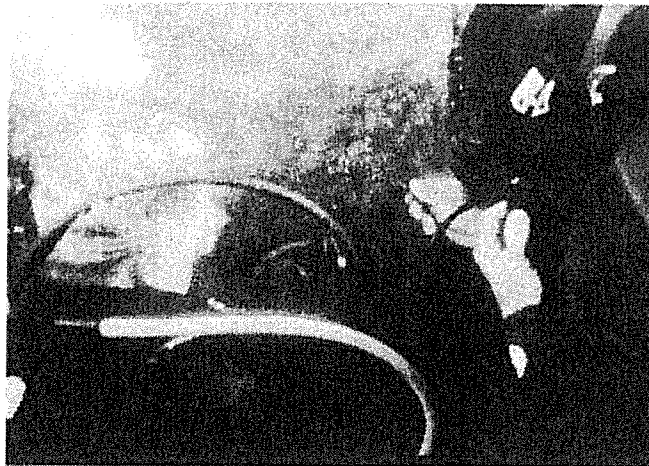
FIGURE 1

iron-based alloys such as steel produces an oxygen barrier and limits oxygen reduction.[3] Oxygen is depleted in the microenvironment, chloride ions diffuse inward, and the pH drops to 4 or less as a result of hydrolysis reactions such as the following:[3]

$$Fe^{+2} + 2\,H_2O + 2Cl^- \rightarrow$$
$$Fe(OH)_2 + 2HCl \qquad (1)$$

The concretion acts like a semipermeable membrane with an electrical resistivity of 2,000 Ω-cm when wet in seawater.[4] Over time, as the concretion thickness increases, the cathodic reactions migrate into the concretion rather than remaining sited at the metal surface. Because the concretion is conductive, the cathode reaction can be spatially separate from the anode reaction. The iron corrosion products interact with the skeletal material, predominately calcite $(CaCO_3)$. Fe^{+2} and Fe^{+3} diffuse into this material and produce chemical changes in the concretion. Concretions, containing up to 10 wt% iron sulfide (FeS) and elemental sulfur, suggest the presence of sulfate-reducing bacteria (SRB). Normally, hydrogen reduction in support of corrosion is a slow process; however, it is stimulated in the presence of SRB.[5] The influence of microbiologically influenced corrosion (MIC) is evident, however, and is under study by Pamela Morris at the Medical University of South Carolina (Charleston, South Carolina).

Macleod[6] describes taking in situ E_{corr} measurements at the metal/concretion interface by drilling through the marine growth or concretion and inserting a pH electrode into the hole. A reference electrode (silver/silver chloride [Ag/AgCl]) is placed adjacent to it. E_{corr} is read on a voltmeter and pH was determined directly at the metal surface by placing a pH probe in the same hole.

Divers taking E_{corr} measurements on the USS *Arizona.* NPS photo by Brett Seymour.

In Pearl Harbor, water exchange with the open ocean is relatively slow. The residence time of water within the harbor has been estimated at ~6 days maximum for bottom water and 1 to 3 days for surface water. Water temperature varies annually from 23 to 29°C (73.4 to 84.2°F), and salinity ranges from 10 to 37% (mean 33%). Salinity is defined as the total amount of dissolved salt, in grams, in 1,000 g of water. The primary effect of salinity is to promote conductivity in seawater.[7]

Experimental Procedures

The UNL Metallurgical Engineering Group made its first observation dive in September 1999 with assistance from divers and archeologists from the USS *Arizona* Memorial and Submerged Resources Center. These observations revealed, as was established by NPS in the 1980s,[2] that the hull is nearly totally encapsulated by concretion varying in thickness from 3 mm to more than 50 mm. Disturbances by divers' movements occasionally initiate the release of gases.

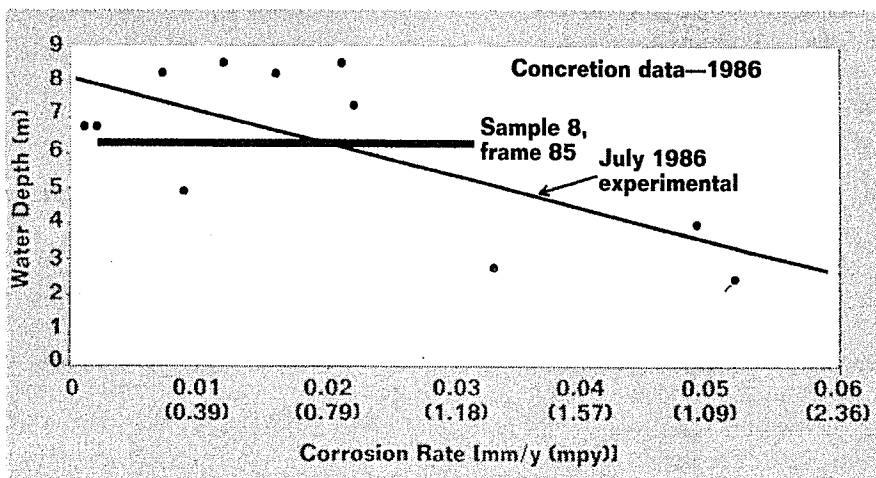Postfield operation discussions in November 1999[8] provided details that facilitated planning for the next field operation in September 2000. A drill rig assembly and depth gage were developed that are now used to drill 1/2-in. (1.3-cm)-diameter holes for insertion of E_{corr} and pH probes. Typical measurement procedures at a given depth include: 1) obtain surface pH; 2) drill to a depth of 10 mm, take pH reading at the bottom of the hole; 3) drill to 18 mm, take pH reading; and 4) drill to metal surface, take pH and (Ag/AgCl) E_{corr} reading (Figure 1). Only one E_{corr} measurement was taken for each drill sequence because the probe needed to be grounded to the hull metal to obtain a reading.

FIGURE 2

Corrosion rate from concretion data (1986) and Hull sample (1988).

FIGURE 3
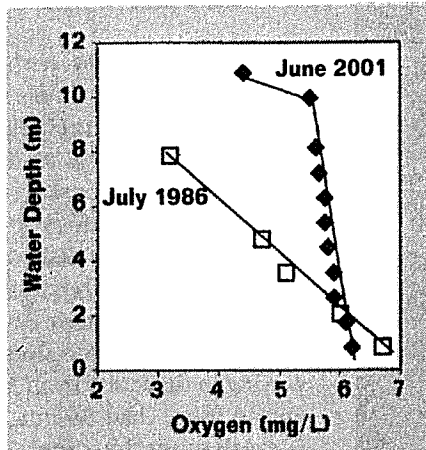
Oxygen concentration as a function of depth: 1986 and 2001.

FIGURE 4

Corrosion potential and corresponding pH as a function of concretion thickness data; taken September 2000.

FIGURE 5

Relationship between pH and concretion thickness data taken September 2000.

Results and Analysis

Samples of concretion were taken in July 1986 from station locations established during survey and mapping of the hull during the 1980s.[2] Each sample contained material removed from a 6-by-6-in. (15-by-15-cm) area of the hull. The samples were dried, ground to fines, and dragged with a magnet to separate the magnetic fraction—primarily magnetite (Fe_3O_4) entrapped in hematite (Fe_2O_3).[2] Figure 2 presents corrosion data from reference 2. Based on these data, corrosion rate is dependent upon water depth; this is consistent with the decrease in oxygen availability with depth as shown for oxygen concentration data taken in July 1986 (Figure 3). Recent oxygen concentration data taken in June 2001, and also plotted in Figure 3, show only a slight decrease in oxygen concentration with depth. The biodiversity study in Pearl Harbor[7] indicates that environmental conditions have improved. Oxygen concentration decreases only slightly based on June 2001 data. This decrease probably resulted from the increase in pressure with depth.
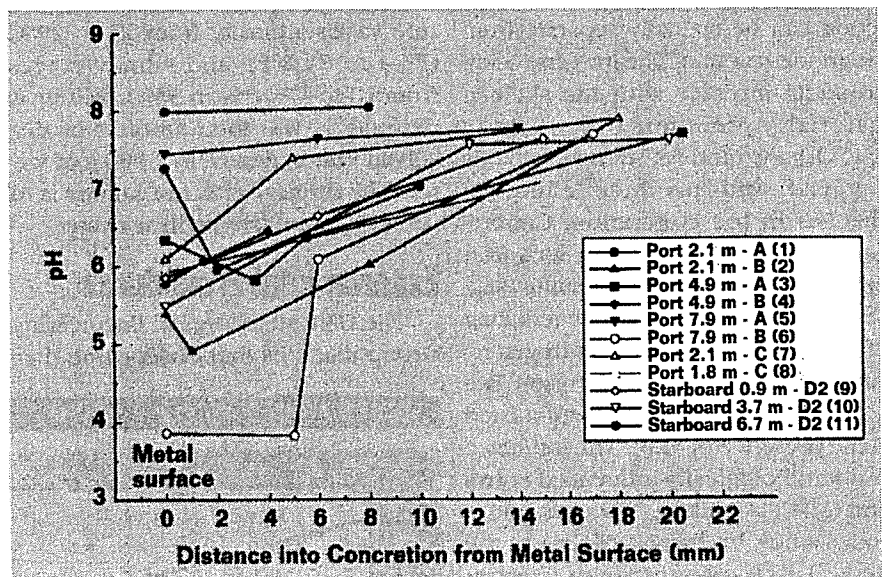
A metal sample, obtained from Frame 85 near the midship area at a water depth of 6.7 m, was delivered to the authors' laboratory in September 1998. With the recent acquisition of detailed structural drawings used during construction of the *Arizona* be-

tween 1914 to 1916 and reconstruction between 1929 to 1931,[9] the investigators determined that the original source of the sample was 25-lb (11.3-kg) plate—equating to a nominal thickness of 0.6 in. (14.9 mm). The thickness after removal from the site varied from 0.5 to 0.6 in. (13 to 15 mm). A metal loss of between 0.002 to 0.07 in.

(0.005 to 1.8 mm) is equivalent to a penetration rate of between 0.001 to 0.031 mm/y. These data, superimposed on Figure 2, are consistent with corrosion rate from weight gain in the concretion at that depth.

Prior to the September 2000 field operation, archival drawings[9] and 1942 damage drawings were used to select

EXPERIMENTAL DATA, FRAME 85, PORT AND STARBOARD

Sample Number[A]	Side[B]	Water Depth (m)	Drill Depth (mm)	Depth from Metal Interface (mm)	pH	E_{corr} (mV, Ag/AgCl)
+14A	Port	2.1	8	0	7.99	-558
(1)	Port		0	8	8.05	
+14B	Port	2.1	18	0	5.39	-590
(2)	Port		17	1	4.91	
	Port		10	8	6.02	
	Port		0	18	7.89	
+5A	Port	4.9	20.5	0	6.34	-564
(3)	Port		17	3.5	5.82	
	Port		14	6.5	6.37	
	Port		0	20.5	7.70	
+5B	Port	4.9	17	0	5.77	-578
(4)	Port		15.5	1.5	6.07	
	Port		13	4	6.46	
	Port		0	17	—	
-5A	Port	7.9	14	0	7.44	-572
(5)	Port		8	6	7.64	
	Port		0	14	7.77	
-5B	Port	7.9	17	0	3.86	-581
(6)	Port		12	5	3.83	
	Port		11	6	6.09	
	Port		0	17	7.69	
+14C	Port	2.1	18	0	6.09	-598
(7)	Port		13	5	7.39	
	Port		0	18	7.89	
+15C	Port	1.8	15	0	5.92	-591
(8)	Port		0	15	7.80	
+14D2	Starboard	0.9	15	0	5.85	-602
(9)	Starboard		9	6	6.65	
	Starboard		0	15	7.64	
+5D2	Starboard	3.7	20	0	5.48	-566
(10)	Starboard		8	12	7.56	
	Starboard		0	20	7.62	
-5D2	Starboard	6.7	10	0	7.26	-554
(11)	Starboard		8	2	5.96	
	Starboard		0	10	7.03	

[A]Elevation (+) above, (–) below top of blister (Figure 6).
[B]Port-top of blister to water surface –21 ft. Starboard-top of blister to water surface –17 ft.

sites for E_{corr} and pH as described earlier.[4,6,10] Site selection took into consideration the avoidance of fuel oil tanks or fuel oil leaked into adjacent or upper compartments—hence the choice of Frame 85. Sample 8 was obtained 2.1 m below the blister top starboard (right). During the 1929-1931 rebuild, the torpedo blister was added to the sides of the hull as protection against torpedoes. Table 1 presents E_{corr} and pH data from the September 2000 field operation. E_{corr} at the metal/concretion interface becomes more negative as the thickness of the accumulated concretion increases. Figure 4 shows a plot of concretion thickness vs E_{corr} with corresponding pH readings. Concretion thickness was determined from the depth of the drill hole to hull

metal as tabulated in Table 1. The pH measurements were obtained at each drill depth and are plotted in Figure 5. On a Pourbaix diagram for iron/water, all of the data points fall within the region where corrosion is active. According to MacLeod,[10] a more negative corrosion potential indicates a lower corrosion current. Although this finding is consistent with reduced oxygen availability under thicker concretions, it is inconsistent with reduced pH and conventional interpretation of the sign.

Hydrogen discharge according to the reaction $2H^+ + 2e^- \rightarrow H_2$ correlates with observations of gas evolution after first penetration into concretion.[4] With respect to the *Arizona*, concretion thickness—hence pH—is independent of water depth and gas release is random. A recent documented example of this occurred during the June 2001 field operation in 3 m of water when drilling penetrated concretion without contacting base metal. Upon withdrawal of the drill, clear water flowed out of the drill hole and then mixed with seawater. This outflow became cloudier and redder and visibility was reduced to <1 ft (0.3 m). The outflow was strong and streamed out the hole ~50 cm. The source of pressure is most likely hydrogen gas. Based on the Nerst equation at pH = 3.9 and E_{corr} = –368 mV (H^+/H), th· partial pressure of H_2 (pH) could e. ceed hundreds of atmospheres as concretion blistered away from the hull and created a gap.

Conclusions

Based on data obtained in 1986, the corrosion rate decreases with water depth. The oxygen concentration measured in 1986 decreased by a factor of two or more, possibly explaining the effect of depth on the corrosion rate observed at that time.

From a compilation of data obtained in September 2000, E_{corr} is dependent on concretion thickness. The concretion, as a barrier to oxygen diffusion, reduces oxygen availability at the metal surface. The crevice effect decreases pH at the concretion to the metal/concretion interface. Three interdependent factors control the corrosion process: hydrogen discharge, oxygen availability, and transportation of iron ions from the metal into the concretion. How these factors interact is not well-understood, but they may be related to the spatial separation of reactions in the concretion.

Corrosion rate data based on direct measurements are very limited at this time, and they afford only an estimate. Below a water depth of ~6 m, the corrosion rate is <2.5 mpy (0.06 mm/y). Wave and tidal effects may increase these rates by a factor of two nearer to the surface.

Work in Progress

Field operations, which resumed in June 2001, incorporated grounding the exterior to the Ag/AgCl probe—allowing E_{corr} as well as pH to be measured as a function of depth into the concretion. As before, final readings were taken at the bottom of the drill hole in contact with hull metal. Assuming that the anode reaction remains at the metal surface whereas the cathodic oxygen consumption reaction migrates to the concretion/seawater interface, the calculated potential gradient is 1.2 mV/mm of concretion thickness. This gradient is equivalent to a relative corrosion rate of 2.7 mpy (0.07 mm/y), somewhat higher than the values given in Figure 2. This rate is based on an electrical resistivity of 2,000 Ω-cm for the concretion.

X-ray diffraction analysis of concretion samples from hull side to water side reveal variations in the amounts of hematite, magnetite, calcite, siderite ($FeCO_3$), and FeOOH. The presence of siderite suggest that iron ion exchange with calcium in the concretion may be partially rate-limiting. Chemistry and structural observations using scanning electron microscopy imaging and electron dispersive spectroscopy element identification are in the planning stages. These studies are being conducted at the Graduate Engineering and Research Center, University of Florida (Gainesville, Florida).

Acquisition of hull core samples at selected areas is planned for late 2002. These samples will permit direct measurement of hull thickness and an independent determination of corrosion rate from comparison with original thickness. Optical and electron microscopy examination and x-ray analysis of these samples will follow.

Acknowledgments

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