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TECHNICAL COMMUNICATION

The Secant Rate of Corrosion: Correlating Observations of the USS *Arizona* Submerged in Pearl Harbor

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Contrary to previous linear projections of steel corrosion in seawater, analysis of an inert marker embedded in USS *Arizona* concretion since the 7 December 1941 attack on Pearl Harbor reveals evidence that the effective corrosion rate decreases with time. The secant rate of corrosion, or *SRC* correlation, derived from this discovery could have a significant impact on failure analysis investigations for concreted shipwrecks or underwater structures. The correlation yields a lower rate of metal thinning than predicted. Development of the correlation is described.

INTRODUCTION

The battleship USS *Arizona*, of riveted low carbon steel construction, was commissioned in 1916. Modernization in 1930 included addition of welded torpedo blisters, replacement of cage masts with tripod masts, additional armor and new armaments. The ship joined the Pacific Fleet at Pearl Harbor in 1940. During the 7 December 1941 Japanese attack, USS *Arizona*, moored in battleship row, was hit by several bombs. The mortal blow came minutes later when a 1760-pound bomb penetrated the deck near turret no. 2 and exploded sympathetically, detonating the ship's forward magazines. The hull was relatively undamaged aft. Much of the forward interior structure was destroyed, including a parting below the barbette of turret no. 1. A total of 1177 sailors and Marines aboard the ship were killed. The ship now rests in about 30 feet of water and 25 feet of sediment with the sediment line approximately at the same level as the original water line.

Approximately 2500 tons of fuel oil still remain aboard ship, either in fuel bunkers or trapped in compartment overheads. Since 2001, research has focused on determining the rate of hull and structural member thinning and incorporating the results into a finite element model (FEM).[1] The goal is prediction of time to failure with attendant release of fuel oil from the *Arizona* into Pearl Harbor. The following sections describe the basis for the secant rate of corrosion (*SRC* correlation) and provide comparison with a linear model of metal thinning.

DATA ACQUISITION

Event Marker

Analysis was based on data at 19.5 feet (6 m) since characterization of concretion sample ASAR 01-1045 was available. This sample was taken one foot aft of frame 75 and one foot above the torpedo blister in December 2001. The dissolved oxygen (DO) at that depth was 41% at 33% salinity and 28°C.[2] Environmental scanning electron microscopy and energy dispersive spectroscopy (ESEM/EDS) studies of the sample identified the concretion chemistry using point and selected area element distribution.[3,4]

A thin layer of presumed silica and alumina particles is shown in Fig. 1. This layer was observed in cross sections of several concretion specimens. The electron backscatter images were overlaid with silicon and aluminum maps. Pearl Harbor sediment was forced onto and attached to a somewhat roughened painted surface of the *Arizona* hull by blasts occurring during the attack. The sand layer became

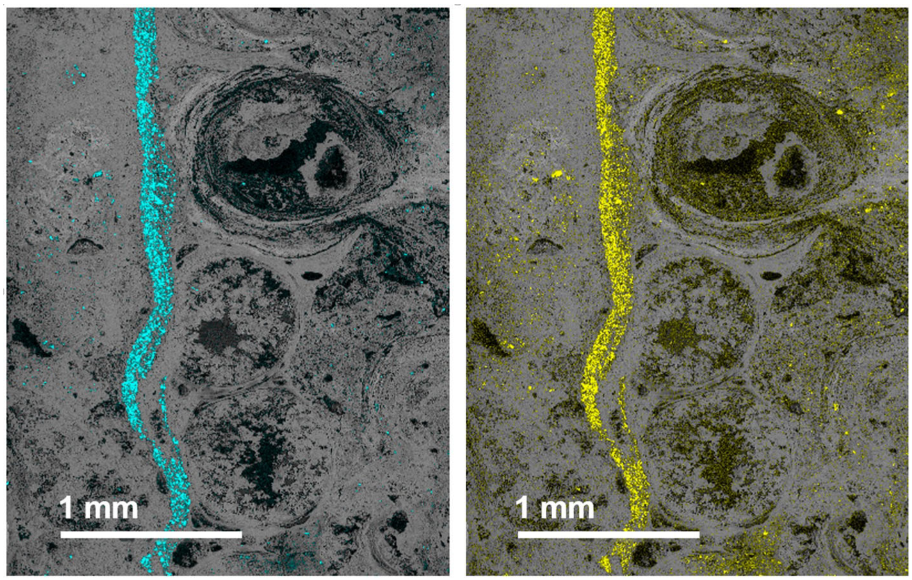

Fig. 1. Silicon marker (left) and aluminum marker (right) with the hull at the left edge of each image. 2002 concretion sample ASAR 01-1045.

an inert marker of the event. The marker could not have existed before the sinking because the sample location was above the water line before 7 December 1941. Confirmation of the source of the particle layer was determined from sediment samples taken from the bottom of the harbor adjacent to the hull of the *Arizona*. The sediment specimens were washed and dried. When observed on the ESEM, they were found to contain silica and alumina particles of the same chemical compositions as determined by EDS. The particle size distributions were also similar.

The silica-alumina marker was embedded within the concretion and consequently offset from the corrosion interface at the time of sampling. This offset suggests a phenomenon similar to the Kirkendall effect, wherein an inert marker placed at a bi-metal interface becomes offset from the interface as the vacancies and marker diffuse in opposite directions.[5] Differences in the rates of diffusion of the primary species cause the marker to shift because of a greater mass transfer in one direction. In the present case, the mechanism of offset begins with rapid early-stage metal loss. The metal is replaced by a precursor to the concretion, an exoskeleton. As calcium migrates to the metal side and iron ions rapidly diffuse to the seaside through the low resistance of the exoskeleton, the concretion matures. The marker is cathodic to iron and remains stable.[6] The end of early-stage metal loss is marked by the densification of the concretion, whereby iron diffusion toward seaside is slowed and the reverse diffusion of calcium, needed for further metal-side growth of the concretion, ceases almost entirely. Calcium migration and the associated concretion growth continue toward seaside.

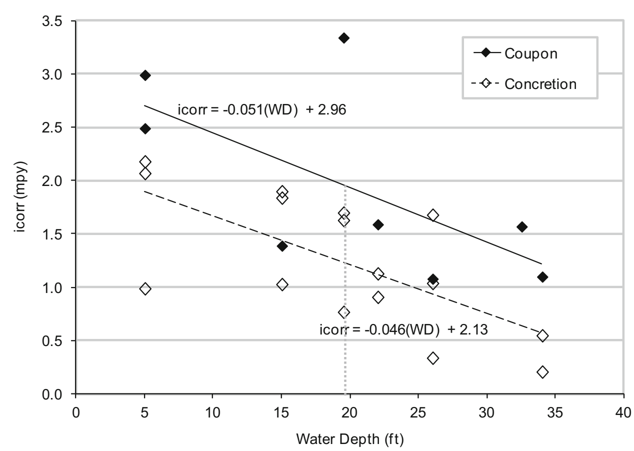

Fig. 2. Corrosion rate as a function of water depth. Coupon (Filled diamond); CECR (Empty diamond).

The silica-alumina marker was embedded to a depth of 35.4 mils (0.9 mm). The embedded depth was assumed to be the extent of metal thinning during the first 1 to 2 years. The form of the corrosion of low carbon steel in seawater is uniform; hence, the term thinning or metal loss is used to express the progress of corrosion over time.

Linear Corrosion Rate

In 2002, the corrosion rate of the *Arizona* hull after 61 years of submergence was determined from composite metal/concretion coupons. The upper solid line in Fig. 2 shows the corrosion rates from metal loss. Due to approval constraints at the USS *Arizona* Memorial, only eight core samples could be obtained. The high variance in corrosion rates from

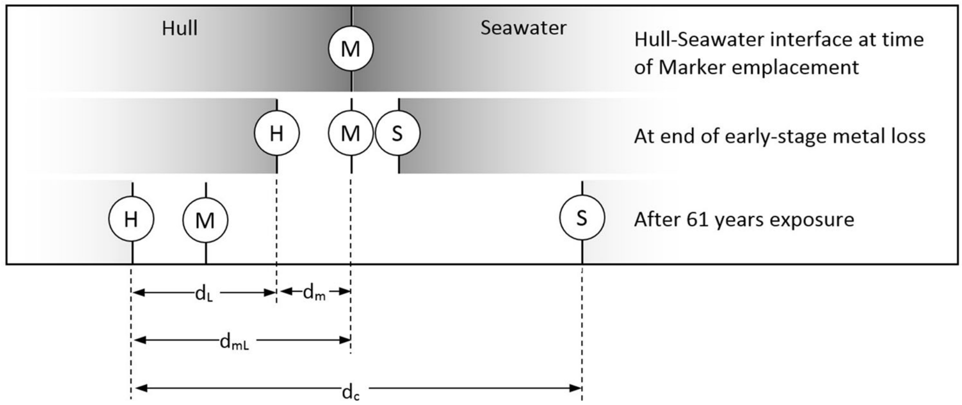

Fig. 3. Time-wise representation of interface and marker locations with the hull oriented to the left, as in Fig. 1. The locations of the inert marker (M), hull interface (H), and seawater interface (S) are depicted at three points in time, namely, the time of marker emplacement, the end of early-stage metal loss and after 61 years.

metal core measurements was accepted in view of the somewhat lower variance and reasonable correlation with concretion analysis as determined by the the concretion equivalent corrosion rate (CECR). The lower dashed line shows the corrosion rates from the CECR.[7,8] At a depth of 19.5 feet (6 m), the corrosion rate from metal loss directly under the concretion sample is 2.0 mpy (0.051 mmpy) and the CECR is 1.3 mpy (0.033 mmpy) where mpy is mils or thousandths of an inch per year and mmpy is millimeters per year. The reasons for separation between the two trend lines are (1) higher initial (pre-concretion) corrosion rates almost certainly produced soluble iron that was not incorporated into the concretion and (2) formation of an oxide layer between the steel surface and the concretion, which strongly adheres to the hull and is not captured during concretion removal and is not included in the analysis. The corrosion rate determined from metal core analysis is greater than the CECR by a factor of ~ 1.6 at 19.5 feet (6 m). This ratio was accepted as the best overall correlation and is factored into the expression for CECR.[8] Based on the expression for the metal core given in Fig. 2, the corrosion rate is 1.97 mpy. The rate was rounded to 2.0 mpy, a value considered valid to base the total metal loss on for extended exposure times.

ANALYSIS

From the solid (coupon) line in Fig. 2 at water depth of 19.5 feet (6 m),

$$d_{\mathrm{mL}} = 2.0 \cdot t. \tag{1}$$

From observation of samples collected at this depth, the total concretion thickness is $d_c = 709$ mils (18 mm). Depth of the marker into concretion from shipside is d_m = 35.4 mils (0.9 mm) and is the thickness of early-stage metal loss. d_L is the thickness of metal loss subsequent to the early stage. d_{mL} is total metal loss during the 61 years from 1941 to 2002,

$$d_{\mathrm{mL}} = d_{\mathrm{m}} + d_{\mathrm{L}}. \tag{2}$$

These quantities are represented graphically in Fig. 3.

Equation 1 provides an estimate of the total metal loss after 61 years:

$$d_{\mathrm{mL}} = 2.0 \text{ mpy } \times 61 \text{ years } = 122 \text{ mils (3.1 mm)} \tag{3}$$

since d_m and d_{mL} are known, Eq. 2 is rearranged to determine d_L,

$$d_{\mathrm{L}} = 122 - 35.4 = 87 \text{ mils (2.2 mm)}. \tag{4}$$

The corrosion rate, excluding the early-stage loss, should agree with CECR if two key assumptions are valid: that (1) the inert marker identifies the original surface of the hull before the sinking and (2) the embedded depth of the marker, d_m, corresponds to early-stage metal loss. These allow estimation of the corrosion rate subsequent to early-stage loss,

$$d_{\mathrm{L}}/61 = 87/61 = 1.42 \text{ mpy (0.036 mm)} \tag{5}$$

Comparison shows good agreement between the CECR of 1.3 mpy (0.033 mmpy) from Fig. 2 and 1.42 mpy (0.036 mmpy) from Eq. 5.

Summing the contributions of the early and subsequent stages of metal loss yields an expression for overall metal loss (ML),

$$\mathrm{ML} = 35.4 + 1.42\,t\,(\text{mils}) = 0.9 + 0.036\,t\,(\text{mm}). \tag{6}$$

The slope of any straight line extending from the origin to a point on this curve comprises the apparent or *secant* rate of corrosion. Dividing both sides of Eq. 6 by the time, t, provides a relationship for the secant rate or corrosion, i_{src},

$$i_{\mathrm{src}} = 35.4/t + 1.42(\text{mpy}) = 0.9/t + 0.036\,(\text{mmpy}). \tag{7}$$

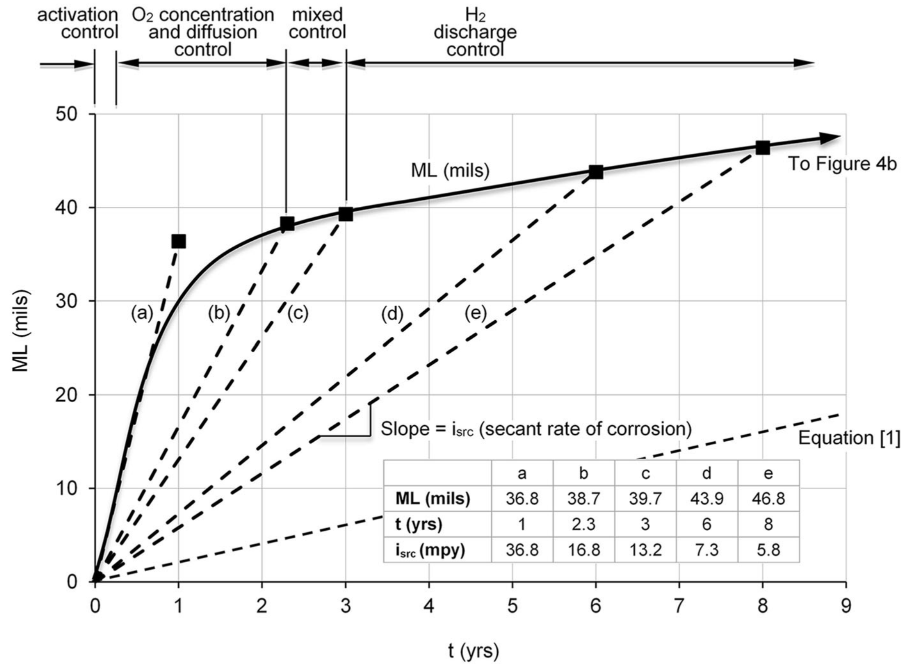

Fig. 4. Projected non-linear corrosion rate depicting the first 8 years after the USS *Arizona* was sunk on 7 December 1941.

This is equivalent to the corrosion rate determined from the thickness loss of hull metal coupons (Fig. 2).[9] As t increases, the first term continues to decrease with the result that i_{src} approaches 1.42 mpy (0.036 mmpy) after very long-term exposure.

The projected corrosion rates to the 8th year are illustrated using a combination of the metal loss, ML, Eq. 6, and the secant rate of corrosion, i_{src}, Eq. 7, in Fig. 4. i_{src} is shown as diagonal dotted lines a through e. These lines intersect ML at calculated times shown on the ML profile. The decrease in slope of the secant lines illustrates the decreasing corrosion rate with time. Values of selected secant rates are listed in the table embedded in the figure. Adopted from Melchers,[10] four early-stage processes are identified: (1) activation, (2) diffusion, (3) mixed diffusion and anaerobic or hydrogen discharge and (4) hydrogen discharge. The estimated time intervals for each process are shown at the top of the profiles. Gas discharge, observed by divers during *Arizona* field operations, indicates sulfate-reducing bacteria stimulating hydrogen evolution.[11,12]

The linear corrosion rate, Eq. 1, appears near the bottom of Fig. 4. It is also shown in Fig. 5 as secant a. Metal loss according to the linear model is less than in the non-linear model in the first few years, but eventually predicts a metal loss that exceeds the non-linear rate of corrosion.

Secant a in Fig. 5 depicts the linear corrosion rate, i_{corr} = 2.0 mpy (0.051 mmpy). Secant a intersects ML at year 61. Secant d extends the corrosion rate and metal loss to 240 years, a time interval predicting major evidence of structural failure.[1] Metal loss in 240 years, from Eq. 1, is 480 mils (12.2 mm), whereas metal loss in 240 years, Eq. 7, is 377 mils (9.6 mm). The decrease is about 22%. The decreases in metal loss for the non-linear model compared to the linear model in the time period between 61 and 300 years are listed in Table I.

DISCUSSION

Until the discovery of the marker, there had been little basis to question assumptions of linearity when interpreting corrosion rates from the USS *Arizona*. Examination of Eq. 7 reveals that as time approaches infinity, the first term approaches zero, resulting in a terminal corrosion rate of 1.42 mpy (0.036 mmpy). Figure 1 shows that the corrosion rate determined from the analysis of the concretion is i_{cecr} = 1.3 mpy (0.033 mmpy). The close agreement between these values supports assumptions pertaining to the origin and location of the silica-alumina marker and confirms the basis of the *SRC* correlation. The magnitude of early-stage corrosion rates is also consistent with the report by Melchers.[10]

Although the terminal rate of 1.42 mpy is never reached, second derivative analysis suggests that the terminal rate is approached rapidly. Within 300 years, Foecke[1] predicts 90% metal loss and collapse of the superstructure. The results of the *SRC* model suggests that a ~ 23% reduction in the corrosion rate could extend 90% of the metal loss to an estimated 360 years.

Oxide formation was not isolated from concretion coverage since the focus was to quantify the effect of concretion as a trap for iron reporting as iron oxides or iron carbonate (siderite) in the concretion.[4]

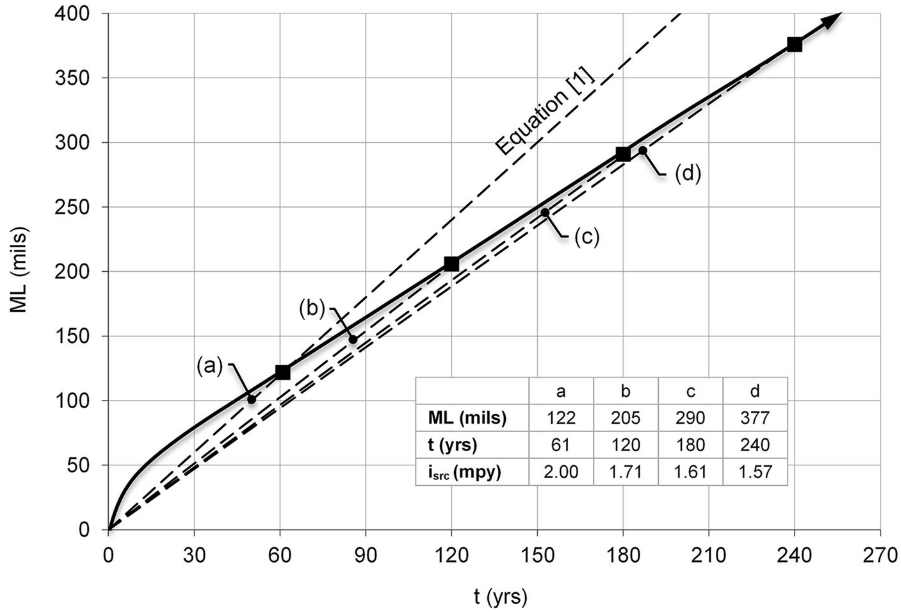

Fig. 5. Projected non-linear corrosion rate depicting years after the USS *Arizona* was sunk.

Table I. Metal loss and percent decrease as shown in Fig. 5

Secant	Time, *t* (years)	i_{corr} mils (mm) equation[1] linear	ML mils (mm) equation[6] non-linear	Percent decrease
a	61	122 (3.1)	122 (3.1)	0.00
b	120	240 (6.1)	206 (5.2)	14.0
c	180	360 (9.1)	291 (7.4)	19.0
d	240	480 (12.2)	376 (9.6)	22.0
Extended	300	600 (15.2)	461 (11.7)	23.0

Recent private communication suggests early corrosion is associated with scale under the event marker with a biofilm over it. The latter prevents loss of scale.[13] ESEM imaging and EDS chemistries identify aragonite, siderite, magnetite, calcium sulfate and akaganeite as iron-bearing minerals present in the concretion. Iron oxides are broadly distributed, whereas calcium is isolated.[4,14]

A comprehensive mass transfer model in which temperature, salinity, oxygen concentration and concretion thickness are the essential variables is beyond the scope of this report. Future work should address those and other factors, including the role of seaside convection, particularly during rapid early-stage metal loss, and the effect of concretion morphology upon subsequent rates of corrosion.[15]

CONCLUSION

Employment of the secant rate of corrosion correlation provides a more realistic rate of corrosion as input to structural failure analysis modeling than that provided by a constant linear corrosion rate. Analysis validates the conclusion that a high early-stage corrosion rate should be considered in assessing when critical metal thinning will result in failure and subsequent hazardous petroleum release or obstruction to sea-going navigation from submerged shipwrecks or structures. The concretion equivalent corrosion rate (CECR) provides a long-term target for corrosion rate prediction after very long-term exposure.

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REFERENCES

1. T. Foecke, L. Ma, M.A. Russell, D.L. Conlin, and L.E. Murphy, *J. Archaeol. Sci.* 37, 1090 (2010).
2. D. Murphy, Private Communication (Sea Bird Electronics, Bellevue, WA 2003).
3. R.J. DeAngelis, in *Structure and Chemical Characterization of Concretion from USS Arizona, Reports 1 and 2* (National park Service Reference H24, (IMRO-SRC) 2012).

4. D.L. Johnson, R.J. DeAngelis, D.J. Medlin, J.D. Carr, and D.L. Conlin, *JOM* 66, 817 (2014).
5. L.S. Darken and R.W. Gurry, *Physical Chemistry of Metals* (New York: McGraw-Hill Book Co, 1953), p. 454.
6. N.A. North, *IJNA* 5, 253 (1976).
7. D.L. Johnson, B.M. Wilson, J.D. Carr, M.A. Russell, L.E. Murphy, D.L. Conlin, *Materials Performance*, 54, (2006).
8. M.A. Russell, D.L. Conlin, L.E. Murphy, D.L. Johnson, B.M. Wilson, and J.D. Carr, *IJNA* 35, 310 (2006).
9. J.E. Johnson, *Private Communication* (Edina: Dow Water and Process Solutions, 2015).
10. R.E. Melchers, *Corrosion* 61, 895 (2005).
11. N.A. North and I.D. MacLeod, *Corrosion of Metals, Chapter 4, Conservation of Marine Archaeological Objects* (Paddington: Butterworth & Co, 1987).
12. J.D. Makinson, D.L. Johnson, M.A. Russell, D.L. Conlin, and L.E. Murphy, *Mater. Perform* 41, 56 (2002).
13. R Sanders, Private Communication United States Coast Guard Academy (2017).
14. B.M. Wilson, D.L. Johnson, H. VanTilburg, M.A. Russell, L.E. Murphy, J.D. Carr, R.D. DeAngelis, and D.L. Conlin, *JOM* 59, 14 (2007).
15. D.L. Johnson, D.J. Medlin, L.E. Murphy, J.D. Carr, and D.L. Conlin, *Corrosion* 67, 125005-1 (2011).