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Advances in Chemical and Structural Characterization of Concretion with Implications for Modeling Marine Corrosion

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The Weins number model and concretion equivalent corrosion rate methodology were developed as potential minimum-impact, cost-effective techniques to determine corrosion damage on submerged steel structures. To apply the full potential of these technologies, a detailed chemical and structural characterization of the concretion (hard biofouling) that transforms into iron bearing minerals is required. The fractions of existing compounds and the quantitative chemistries are difficult to determine from x-ray diffraction. Environmental scanning electron microscopy was used to present chemical compositions by means of energy-dispersive spectroscopy (EDS). EDS demonstrates the chemical data in mapping format or in point or selected area chemistries. Selected-area EDS data collection at precise locations is presented in terms of atomic percent. The mechanism of formation and distribution of the iron-bearing mineral species at specific locations will be presented. Based on water retention measurements, porosity in terms of void volume varies from 15 v/o to 30 v/o (vol.%). The void path displayed by scanning electron microscopy imaging illustrates the tortuous path by which oxygen migrates in the water phase within the concretion from seaside to metalside.

INTRODUCTION

Seventy years is a long time and there aren't that many people left today who remember the attack on Pearl Harbor by Japanese aircraft, and the subsequent sinking of the *USS Arizona*. The first author remembers and has been privileged, along with a dedicated research team, to contribute to a legacy of science and an already established *USS Arizona* legacy of valor and history. The purpose of this article is to describe the structure and chemistry of that most unlikely source of scientific inquiry, hard biofouling (concretion) removed from the *USS Arizona* hull. Also, described for the first time is documentation, revealed by environmental scanning electron microscopy (ESEM) concretion imaging, of the munitions explosion that destroyed the *USS Arizona*.

As marine biofouling accumulates on submerged shipwrecks over time, it leaves behind a track of

evidence: a hard, relatively compacted layer often referred to as concretion because of appearance and aggregation much like that of concrete. Biofouling and associated microbiologically induced corrosion (MIC) on steel and iron base vessels and structures has been the subject of extensive study over a period of many years.¹⁻⁶ These studies have been significant in evaluating cause and effect and in describing remedial efforts to minimize marine corrosion. Recently published concretion equivalent corrosion rate (CECR) methodology carries these studies further by using the chemical and physical properties of the concretion to determine the corrosion rate.^{7,8} The Weins Number concept (Wn) is a follow-on to CECR. The idea behind the Wn concept is a means to correlate corrosion rate and environmental parameters at each site and to tie these sites together in a linear profile based on absolute reaction rate theory.^{9,10} Using these methodologies,

corrosion rates are determined under conditions that would otherwise be difficult and expensive to determine by conventional means. To apply the full potential of CECR and the Wn concept, chemical and structural characterization of the concretion that transforms into iron minerals is required.

REVIEW

Structural and Chemical Characterization

Analytical x-ray diffraction (XRD) identifies the crystalline compounds existing in concretion separately or in a mixture of compounds.^{6,11,12} Structural characteristics determine that (FeOOH) goethite, FeCO₃ (siderite), CaCO₃ (aragonite), and Fe₃O₄ (magnetite) were the primary minerals present in *USS Arizona* concretion. However, the fractions of existing compounds and the quantitative chemistries could not be determined from x-ray data alone. Initially, chemistries of the *USS Arizona* concretion were determined by ESEM.¹¹ Iron contents across the concretion varied from 18 wt.% to 65 wt.%. Graphical integration of point data varying from 18% to 65% revealed a mean iron content of approximately 50 wt.%, which is in good agreement with total iron contents determined from direct wet chemical analysis.⁷ The wide spread in data at any one site has been suspected to be caused, at least in part, by inhomogeneities in the concretion and the resulting spread in diffusion effective concretion thickness.¹⁰ Better information is needed about the structure and chemistry of concretion to make a more accurate assessment of this parameter. ESEM in this investigation was carried one step further by incorporating energy-dispersive spectroscopy (EDS). The result demonstrates the chemical data in mapping format or in point or area selected chemistries. The void path is revealed by vacuum impregnating the concretion and SEM imaging. This observation illustrates the tortuous path through which oxygen diffuses in sea water trapped inside the concretion as it migrates from seaside to shipside. A detailed structural characterization and chemistry profile of elemental distribution in concretion with particular emphasis on regions surrounding sea shells, embedded in the *USS Arizona* concretion, is described as follows.¹³

Material and ESEM Specimen Preparation

The concretion sample was obtained near midship on the vertical section of the *USS Arizona* hull. It was sectioned on a fine-toothed band saw into four sections as shown in Fig. 1. The sample in cross section is shown in Fig. 2.

Shell structures are visible in the seaside portion and in the cross-sectional view of the concretion. Considerable void population is also observed in the cross-sectional view in Fig. 2. The smallest piece of the concretion shown in Fig. 1 was prepared for observation on the ESEM.

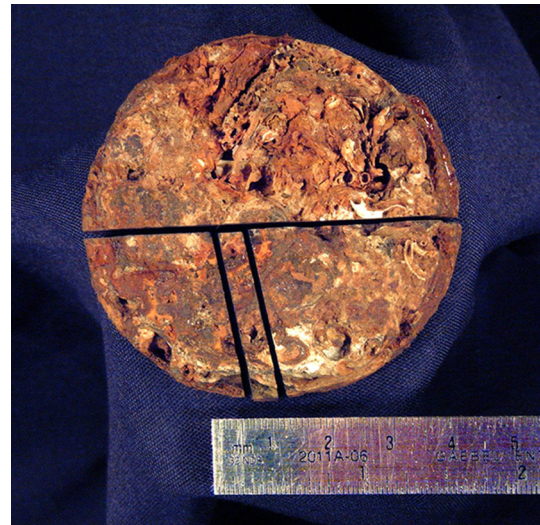


Fig. 1. Photograph of a concretion sample from the *USS Arizona*.



Fig. 2. Photograph of a cross section of the concretion sample.

Initially specimens were prepared by grinding the band saw cut surface on various grits of metallographic grinding paper and were observed employing the ESEM. All attempts at specimen preparation by this method failed to produce a surface suitable for imaging as a result of the high void content and the brittle nature of the concretion. During grinding, the voids would be filled by particles of the specimen being removed. This difficulty was eliminated by filling the voids by vacuum impregnation with an epoxy of high fluidity. The epoxy employed was product No: 813-510 obtained from Ted Pella Inc., Redding, CA, USA. After epoxy impregnation, the cross-sectional surface of the specimen was ground to a 2000 grit finish (about 1 micron particle size) employing a Struers semiautomatic grinding and polishing machine (Struers, Inc., Westlake, OH, USA).

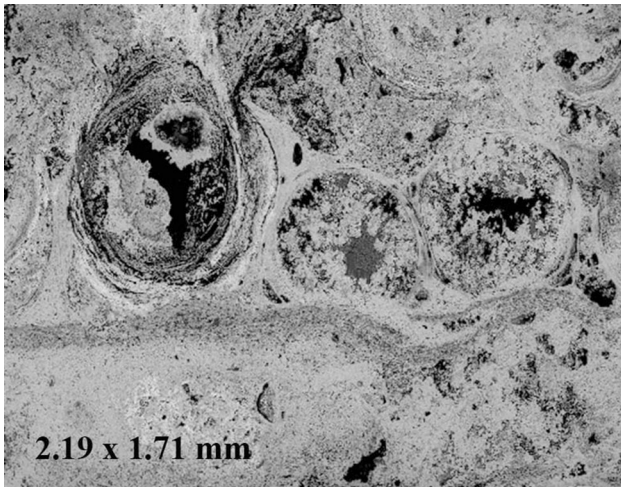


Fig. 3. No overlay. Shippside—bottom.

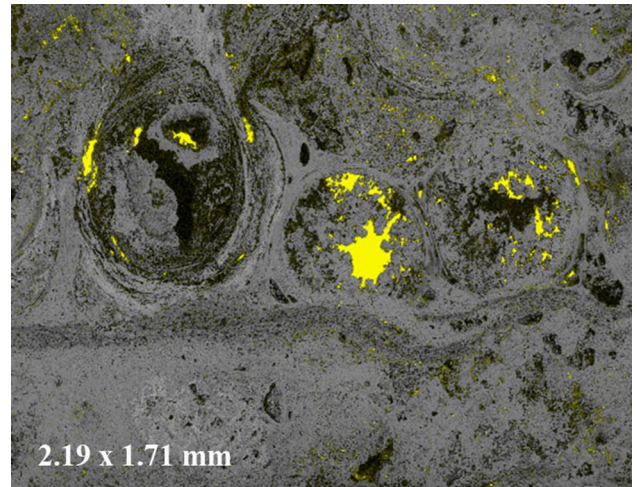


Fig. 5. Sulfur (yellow) map overlay. Shippside—bottom.

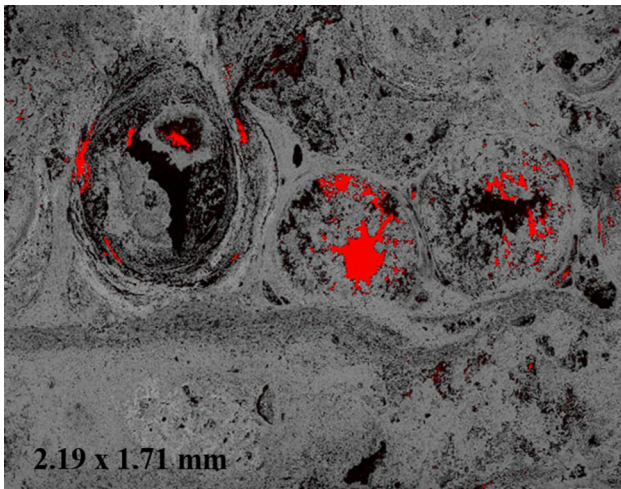


Fig. 4. Calcium (red) map overlay. Shippside—bottom.

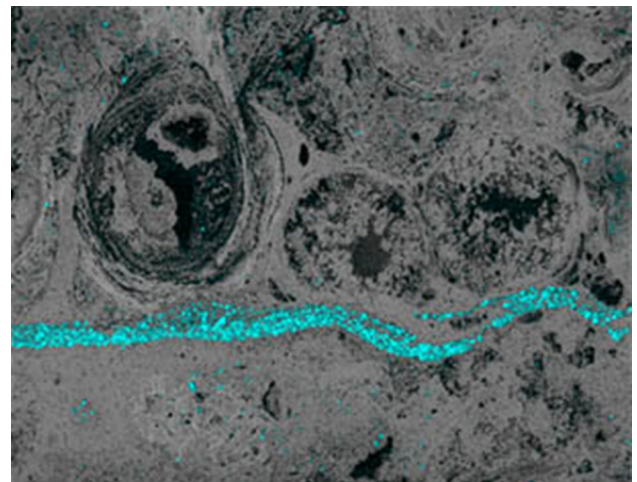


Fig. 6. Silicon (blue) map overlay. Shippside—bottom.

This preparation technique produced specimens of exceptional quality for ESEM imaging and data collection as shown in Figs. 3–12. The brighter contrast regions in the backscatter electron image of the concretion, shown in Fig. 3, are areas containing a high concentration of iron atoms, and the darkest regions are areas high in low-atomic-weight carbon present in the epoxy. The image has excellent definition and detail of the structure of the concretion indicating minimal damage was introduced during polishing. The void regions in the image containing epoxy are shown in red in the carbon map superimposed on the backscatter image, as shown in Fig. 9. Figures 3 through 9 are backscatter images of the exact same area overlaid with elemental maps of calcium Fig. 4, sulfur Fig. 5, silicon Fig. 6, aluminum Fig. 7, iron plus calcium Fig. 8, and carbon Fig. 9. Please note that the shippside position is at the bottom side of each image in Figs. 3–10a and the image size is 2.19 mm × 1.71 mm.

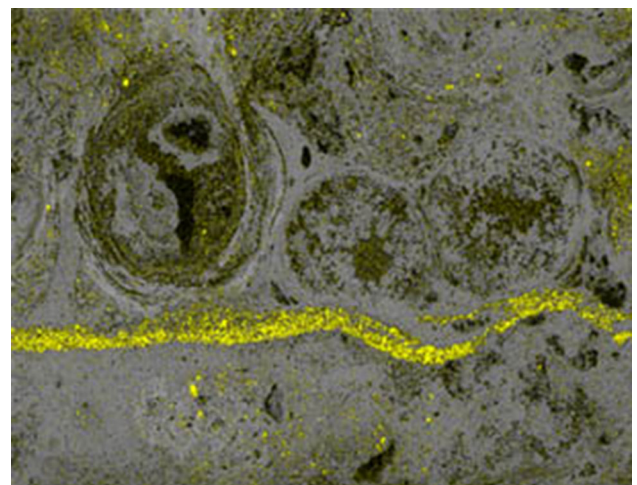


Fig. 7. Aluminum (yellow) map overlay. Shippside—bottom.

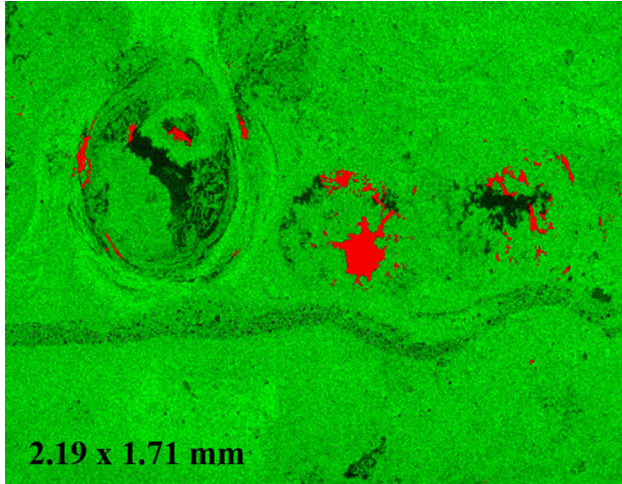


Fig. 8. Iron (green) and calcium (red) map overlay. Shiplside—bottom.

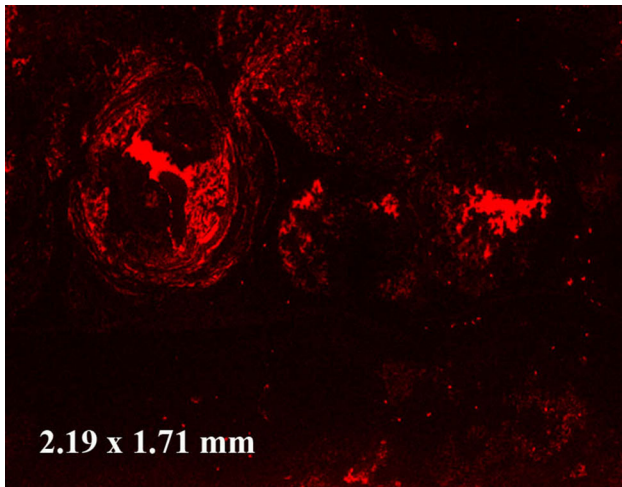


Fig. 9. Voids filled with epoxy showing carbon (red) map. Shiplside—bottom.

Figures 11 and 12 are seaside images, and the image size is 2.36 mm \times 1.8 mm.

RESULTS

Figure 3 illustrates imaging without element identifying overlay. Inhomogeneity in the form of a near-circular embedded shell is noted in at least three locations. Figures 4 and 5 reveal identical overlays for calcium and sulfur indicating that the dominant specie in these areas is a calcium mineral containing sulfur. The specific minerals present are discussed below. Figures 6 and 7 reveal a thin layer of Si and Al, respectively, traversing the concretion cross section. Figure 6 shows the backscatter electron image overlaid with a silicon map. The image with an aluminum map is shown in Fig. 7. The aluminum is in the form of Al_2O_3 and silicon in the form of SiO_2 , which are both compounds found in

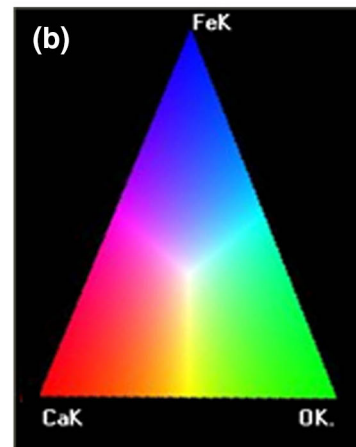
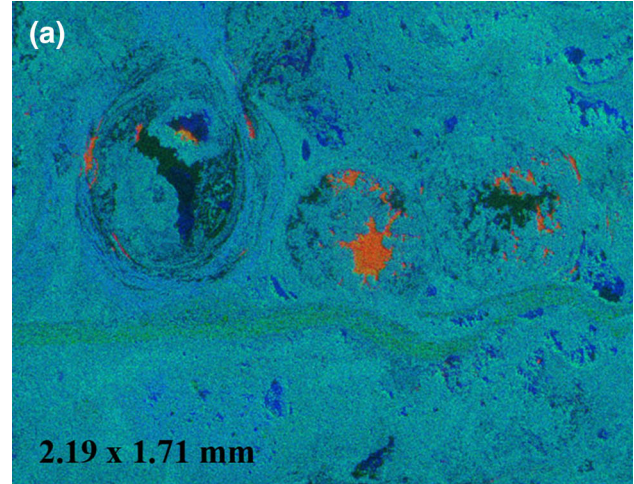


Fig. 10. (a) Calcium (red), iron (blue), and oxygen (green) RGB map. Shiplside—bottom. (b) Elemental combinations for Figs. 10a and 11.

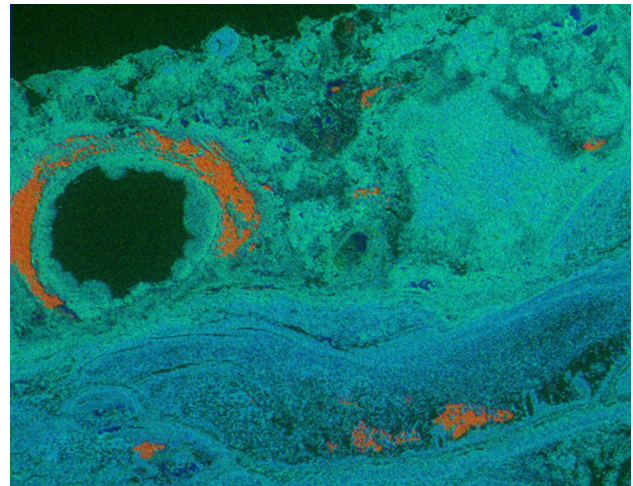


Fig. 11. Calcium (red), iron (blue), and oxygen (green) RGB map. Seaside—top. See Fig. 10b for elemental combinations.

sand. Robert DeAngelis, a co-author, proposed that Pearl Harbor sediment was forced into the surface of the *USS Arizona* hull by blasts occurring during

the attack and that the layer acts as an inert marker. His theory was confirmed from sediment taken adjacent to the *USS Arizona*. Specimens were washed and dried and found to contain silica and alumina particles of the same EDX chemical compositions and size as the particles embedded in the concretion removed from *USS Arizona*. These observations are exciting and point to further research into application of the Kirkendall effect to estimate corrosion rate as a function of the distance between the marker and the existing metal/concretion interface after a 60-year exposure. The Kirkendall effect was first reported from analysis of inert marker transport in metallic alloys.⁹ Figure 8 shows the distribution of iron in the concretion with the exception of regions containing calcium or void

in the vicinity of shell. This image confirms that iron is otherwise relatively uniform in distribution, constituting a primary sink for iron as corrosion proceeds. Such distribution is the basis for the CECR methodology. Figure 9 illustrates the extensive void presence in concretion and confirms calculations showing void volumes as high as 35%. Figures 10a and 10b illustrate complex element combinations, particularly the shades of blue to green representing the various iron oxides that occur throughout the image. Siderite, an iron carbonate, is dominant in XRD scans although it is not isolated in maps associated with backscatter detector images.

Seaside images are similar to shipside images with the dominant presence of iron in the form of oxide minerals, and siderite as has been observed near shipside. Embedded shells tend to concentrate toward seaside as illustrated in Figs. 11 and 12. The coloring of iron oxides in Fig 11 change with increasing distance from seaside from higher oxygen (greenish) to lower oxygen (bluish). Figure 12 clearly shows the dominance of calcium and void in the center surrounded by void and sulfur. This observation has led to a better understanding of iron distribution and avoidance of these areas in determination of oxygen diffusion thickness.

Superimposed on the Fig. 12 image are points at which chemistries were determined by EDS. The chemistries, in atomic percentages, at these locations are listed in Table I. Table II lists the stoichiometric atomic chemistries of identified minerals associated with common steel corrosion products.

A composite Fe + Ca + S, not shown, map shows the complex chemistry associated with the transformation of CaCO₃, aragonite, to FeCO₃, siderite.

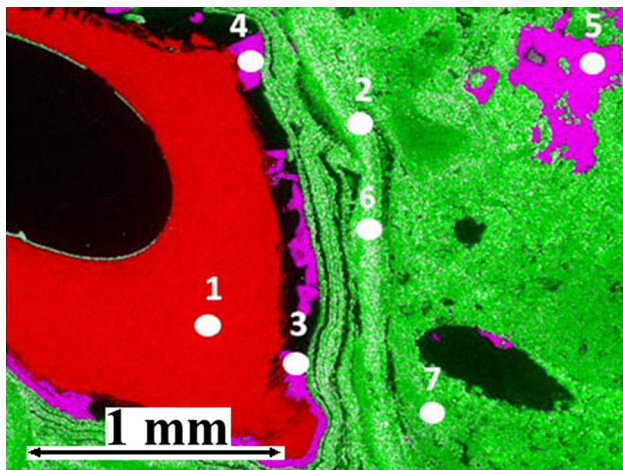


Fig. 12. Shell encased in concretion, calcium (red), iron (green), and sulfur (magenta). Seaside—top.

Table I. Chemistries in at.%, determined by EDS at the positions indicated in Fig. 12

Position	C	O	Al	Si	S	Cl	Ca	Fe
1	22.7	57.7	0.4	0.3	0.3	0.2	17.7	0.8
2	20.9	58.6	0.0	0.4	0.5	1.1	0.5	18.0
3	22.6	54.9	0.1	0.2	10.1	0.1	10.4	1.6
4	23.7	53.6	0.2	0.2	10.4	0.1	10.1	1.8
5	13.0	59.4	0.2	0.2	13.1	0.2	11.5	2.3
6	23.5	57.0	0.1	0.4	0.5	0.7	0.5	17.3
7	36.2	47.2	0.3	0.7	0.9	1.2	0.3	13.3

Table II. Atomic percentages of stoichiometric compounds in concretion formed during the corrosion of steel

Compound	Name	C	O	S	Ca	Fe
CaCO ₃	Aragonite	20	60	0	20	0
FeCO ₃	Siderite	20	60	0	0	20
Fe ₃ O ₄	Magnetite	0	57	0	0	43
CaSO ₄	Ca Sulfate	0	66	17	17	0
FeO(OH)	Akaganeite	0	67	0	0	33

The EDS chemical mapping images are of qualitative value but give only estimates of quantitative chemical compositions. Accurate chemical composition data can be obtained by point or selected area EDS data collection. The carbon at position 7 is much higher due probably to epoxy in contact with porosity.

Comparison of the tabulated data indicates that the composition of the shell at position 1, Fig. 12, is CaCO_3 and that positions 2 and 6 seem to have a composition of FeCO_3 . The latter positions are on portions of the seashell in which the calcium has been replaced by iron originating from the ship. Similarly, based on Tables I and II, calcium sulfate seems to exist in positions 3, 4, and 5. It is assumed that sulfite converts to sulfate in positions rich in oxygen. This raises the question of the source of the sulfur present in these regions. It is also interesting that the CaSO_4 encases the CaCO_3 portion of the seashell. This positioning is easily observed at positions 3 and 4; however, position 5 is at a location on an interface of a shell of a different orientation. Position 7, located in the green area represented by iron, is identified as $\text{FeO}(\text{OH})$ or Akaganeite, a stoichiometry that has been reported on other marine wreck sites as goethite or lepidocrocite,^{12,14} the latter a variable stoichiometry dependent on oxidizing conditions.

CONCLUSIONS

1. Structural characterization and chemical distribution of elements in concretion confirm the viability of the CECR methodology and lead to a better interpretation of the physical properties of concretion used in both CECR methodology and the Weins number model.
2. Information required to obtain more accurate measurements of parameters inserted into the CECR and Wn equations has been applied, particularly that of determination of the effective diffusion thickness through which oxygen migrates from seaside to shipside. To select the best possible regions for cross-section thickness measurements, visual or macrographic examination of the cross sections is recommended to avoid measurements near or over a shell that yield high thickness values in regions void of iron.
3. An unexpected finding in this investigation has been the appearance of a layer of aluminum and silicon embedded in the concretion. The source of these two elements was aluminum and silicon oxides contained in bottom sand and mud samples taken adjacent to the *USS Arizona* Memorial. This evidence indicates that the sands were forced onto the hull surface of the *USS Arizona*, most likely the result of the sympathetic detonation of

USS Arizona munitions from a Japanese aircraft bomb impact. The displacement of the oxides as a marker in the concretion is now under study to determine how the data could be used to determine corrosion rates in substantiation of existing corrosion models.

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