A Simple Technique for the Corrosion Inhibition of Underwater Cannonball from a Shipwreck

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Abstract. This study aims to conserve the underwater cannonball before storing it in a museum. Removing the protective crust of iron artifacts without the correct and proper method can cause rapid corrosion. To prevent damage, artifacts must be conserved in the right solution. Conservation was conducted in four stages during this research project. The first stage is the identification of weathering, and the second stage is the analysis and characterization of the corroded surface using a microscope, XRD (X-ray diffraction), XRF (X-ray fluorescence), and SEM (scanning electron microscopy). The third stage is the passivation/deactivation process, achieved using sodium hydroxide, soapy water and kaffir lime water. The fourth stage is stabilizing/coating the iron cannonball underwater heritage materials as soon as possible using microcrystalline wax to prevent further corrosion. This stage should solve the conservation problems associated with the object so that the object can last for a long time. Dry and wet-activated corrosion was characterized by applying XRD to the obtained mineral akageneite. The akageneite minerals were actively corroded and contained high concentrations of Cl atoms revealing dry and wet activated corrosion of 66.60% and 64.96%, respectively. After being conserved with several steps and NaOH, soapy water and kaffir lime water, inactive corrosion was observed. Based on the results of the analysis performed with XRF, the cannonball does not contain Cl, and the Fe content is 98.99%. The conservation method used in this research is excellent and appropriate for conserving cultural heritage materials, including underwater iron cannonballs.

Keywords: Cannonball; Conservation; Corrosion; Iron; Materials; Underwater

1. Introduction

Indonesia is an archipelago with thousands of islands that have varied cultures. That diversity produces variegated cultural heritage remains, either in the form of objects, structures, buildings, sites, or other heritage types. Based on the material aspects, objects associated with cultural heritage are composed of different materials, including stone, brick, wood, metal, and others. So that future generations can enjoy the culture in conditions that are whole and complete, cultural heritage must be preserved. To preserve cultural heritage, conservation actions are needed (Hamilton, 2010).

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As an archipelago country, Indonesia is also a maritime country with a broad sea region. The history of the nation of Indonesia reflects the marine culture which made a long journey from the Malay Archipelago. This area was an important trade route for a very long time, especially for the trade of commodity spices (Hamilton, 2010). The current marine transportation area allows Nusantara to store a wealth of relics from the past. The richness of the underwater remains due to the sunken ships (shipwrecks), which are very many scattered in various locations, is unknown. In addition to sunken ships, the sea of Indonesia also stores a wealth of other underwater heritage, such as aircraft and other war remnants.

Economically, underwater relics are also high-value, and their protection is threatened (Liu et al., 2011). The conservation method used for underwater relics must pay attention to the characteristics of materials and weathering that occur. Conserved underwater relics should also be handled by planning before the adoption, at the time of appointment, and during transport. Planning the placement of artifacts after their protection is also a concern of the methods determined for conservation. The researchers developing methods of conservation of underwater heritage currently still have work to continue to do (Cornell and Schwertmann, 2003).

The most striking feature of iron corrosion in an underwater environment (sea) is the formation of a thick concretion. Concrete formed on the iron buried beneath the seafloor and exposed to seawater. This process of filling the holes and pores in concretion forms a cement matrix of iron, which slowly dissolves and replaces the original calcite matrix (Liu et al., 2011). During crystallization, in areas with a low oxygen content, the reaction between the iron ions and sulfide (S²⁻) ions occurs due to the sulfate generated from the formation of iron (II) sulfide (FeS) and the element sulfur (Liu et al., 2011).

Several methods have been developed for the conservation of underwater cannonball heritage, such as cathodic protection (Bethencourt et al., 2018; Angelini, Grassini, and Tusa, 2013; Heldtberg, Macleod, and Richards, 2004), aerated and deaerated using NaOH solutions (Kergourlay et al., 2018), using natural products (Abdel-Karim and El-Shamy, 2022; Verma et al., 2017; Palou, Olivares-Xomelt, and Likhanova, 2014; Cano and Lafuente, 2013; Kesavan, Gopiraman, and Sulochana, 2012). Several natural products and chemicals have been used as green corrosion inhibitors, such as anthill (Myrmecodia Pendants) extract (Pradityana et al., 2017); acid medium (Shetty and Shetty, 2017); malonic acid and succinic acid (Thaha et al., 2019). The final stage after corrosion stops on underwater cannonball heritage is coating. Several materials are often used for coatings, such as wax (Ashkenazi et al., 2017) and graphene nanocomposite (Kumar et al., 2022). Some conservation methods that are currently trending are using natural materials because they are nontoxic, cheap, and environmentally friendly.

This paper aims to conserve underwater cannonball heritage. Removing the protective cover crust from iron artifacts without the correct and proper method can cause the artifact to corrode rapidly. To prevent damage, artifacts must be conserved in the right solution. This research aims to stop the corrosion process and conserve iron objects in aqueous alkali solutions, and the potential corrosion was measured.

2. Methods

2.1. Identification of samples

The object examined was the iron cannonball underwater cultural remnants taken from the sea of Batavia/Jayakarta, Indonesia. The identified weathering rates can be compared by paying attention to every object experiencing active corrosion, which is characterized by the emergence of new rust (such as the details of a fluid). Objects undergoing active corrosion
can be grouped and sequenced by implementing appropriate levels of active corrosion handling. The identification of the weathering of the underwater iron relics is observed.

2.2. Analysis and characterization of the iron cannonball surface reveal an underwater culture

The existing components in the sample were studied and characterized using B8 Focus X-ray diffraction (XRD) and portable Olympus X-ray fluorescence (XRF) systems. The corrosion of the object surface was analyzed using a microscope (HMR) and a Jeol JSM-T300 scanning electron microscopy (SEM) system.

2.3. Passivation/deactivation corrosion

The iron cannonball material was immersed in a solution of 5% sodium carbonate (Na$_2$CO$_3$ from Merck, pro analysis grade). The pH was maintained at the alkaline condition in the range of 11-13. If the pH goes down, it should be raised in the field with a solution of sodium hydroxide (NaOH from Merck, pro analysis grade). Soaking was performed about once a week, and the material was then rinsed with water and subsequently distilled water. The next object is dried, its development is viewed if it still happens, and the corrosion process is then repeated. Before the process is complete, passivation does not clean up the crust or rust, and the coating would be a natural protector in the meantime. Next, cleaning was performed manually with a brush, needles, chisel, hammer and other tools. Next, cleanup is at the core of the conservation activities, so the conservation problems should be completed so that the materials can last for a long time. The cleaning process was performed by washing using soapy water until the material was completely clean. Then, kaffir lime water was used to remove the remnants of corrosion and concrete, and later, distilled water was used to clean, rinse, and dry.

2.4. Stabilizing/coating

After all the processes are finished, the metal is still prone to further corrosion. Therefore, stabilization needs to be done as soon as possible. Stabilization is performed by coating. The material used is a commonly used coating material, namely, candle microcrystalline wax. The wax is heated so that it melts, and turpentine solvent is added to the wax to achieve a 5:100 w/v ratio so that the resulting solution is 5% microcrystalline wax (Merck, pro analysis grade). The microcrystalline wax solution was further mounted on the soft iron cannonballs using a brush. Figure 1 shows the schematic procedure of the conservation of underwater cannonball heritage.

![Figure 1](image-url) Schematic procedure of the conservation of underwater cannonball heritage
3. **Results and Discussion**

3.1. **Identification of sample**

The weathering of the iron relics is observed underwater. The result of the identification of the sample is shown in Figure 2. Figure 2a-d shows the weathering and corrosion that occurs on an iron cannonball material through the formation of concretion (a buildup of crust), and the damages cause the breaking and destruction of the objects.

![Figure 2](image)

**Figure 2** Weathering and corrosion of the iron cannonball material (a) low, (b) medium, (c) high, (d) advanced

When iron is exposed to the atmosphere, the environment forms different iron-oxides, such as magnetite (Fe$_3$O$_4$), hematite (α-Fe$_2$O$_3$), and maghemite (γ-Fe$_2$O$_3$) (Cornell and Schwertmann, 2003). At temperatures higher than 560 °C, the general sequence of the iron-oxide layer (from the interior to each surface) is Fe/FeO/Fe$_3$O$_4$/Fe$_2$O$_3$/O$_2$ (Fontana, 2005). The redness of the rust powder and the presence of many cracks and cavities on the object’s surface indicate an active corrosion process being in progress, causing the continuous loss of metals, as well as the degradation of the mechanical properties (Selwyn, 2004). The corrosion of iron-based archeological artifacts immersed in seawater is an electrochemical process involving anodic and cathodic reactions in an aqueous electrolyte environment. Biological processes also involve anaerobic bacteria (Liu et al., 2011). When iron is put into solution, the oxide layer grows slowly, forming oxide compounds, such as goethite (α-FeOOH), akageneite (β-FeOOH), and lepidocrocite (γ-FeOOH) (Balos, Benscoter, and Pense, 2009; Barrena, De-Salazar, and Soria, 2008; Neff et al., 2006a; 2006b; 2005; 2004; Cornell and Schwertmann, 2003; Balasubramaniam, Kumar, and Dillmann, 2003).

3.2. **Characterization of the surface corrosion of iron cannonball materials immersed in water using a handy microscope**

The results of the analysis and characterization of the objects obtained using a handy microscope are shown in Figure 3. Figure 3 can show the presence of corrosion on the immersed iron cannonball, and the corrosion processes can be distinguished into two types, namely, dry active corrosion, as shown in Figure 3a and wet active corrosion, as shown in Figure 3b.

The ongoing problem with iron archeology is the continued corrosion that occurs after excavation, caused by salt accumulation during burial. One way to repair iron cultural heritage material is by immersing the objects in a solution and waiting for chloride ions to spread out (Selwyn, 2004). The weathering of underwater relics generally takes place faster than land-based relics. The rate of the weathering of cultural objects immersed in water can be 5-10 times faster than that of cultural heritage objects on land (Hamilton, 2010).
Figure 3 Handy microscope images showing the corrosion of the iron cannonball material by (a) dry active corrosion and (b) wet active corrosion

3.3. XRD characterization of the surface corrosion of iron cannonball material immersed in water

The result of the characterization of the surface corrosion using XRD has been shown in Figure 4a and Figure 4b. X-ray spectrometry methods such as XRD, XRF, and SEM-EDX/EDS are very suitable for the analysis of inorganic material in the field of conservation and heritage restoration (Emara and Korany, 2016; Theile et al., 2014; Fernandes et al., 2013; Watkinson, 2013; Van-Grieken and Worobiec, 2011). Before carrying out conservation, the material to be conserved must be examined, so it is more appropriate to determine conservation techniques by considering the costs and resources (Argyropoulos et al., 2013).

Figure 4 X-ray diffraction pattern of the cannonball material underwater heritage corroded by (a) dry active corrosion, (b) wet active corrosion

The X-ray diffraction patterns in Figure 4 clearly show the distinction between the compounds contained in the corroded material. As shown in Figure 4a, peaks are observed at 2θ positions of 26.67° and 35.11°, while Figure 4b shows peaks at 2θ positions of 26.67° and 35.17°. These peaks correspond to akageneite, as supported by the research of Gil et al. (2003), who found the presence of akageneite to correspond to the peaks at 2θ = 26.68° and 2θ = 35.18°. The X-ray diffraction results indicate that the sample obtained from the corroded iron contains two types of iron oxide, akageneite and lepidocrocite. The corrosion product of iron-containing chloride ions, for example, is akageneite (Jegdic et al., 2012). In addition to artifact materials, the corrosion process is influenced by environmental pollutants, other archeological materials, geography, the microorganisms in the soil, vegetation, land use, soil chemistry, soil physical properties, and the presence or absence of water and air (Mentovich et al., 2010; Cvikel and Kahanov, 2009; Selwyn, 2004). The mineral composition was obtained from the XRD characterization. The result of the mineral composition investigation is shown in Table 1.
Table 1 Characterization of surface corrosion using XRD

<table>
<thead>
<tr>
<th>No.</th>
<th>Dry active corrosion</th>
<th>Wet active corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mineral</td>
<td>Amounts (%)</td>
</tr>
<tr>
<td>1</td>
<td>Halite</td>
<td>9.12</td>
</tr>
<tr>
<td>2</td>
<td>Akageneite</td>
<td>89.63</td>
</tr>
<tr>
<td>3</td>
<td>Famatinite</td>
<td>0.72</td>
</tr>
<tr>
<td>4</td>
<td>Briartite</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Table 1 shows the presence of minerals in the form of akageneite, which is the most abundant mineral and results from the corrosion of ferrous metals in seawater. Thus, the leading cause of the corrosion of the metal bottom in saltwater is the chloride ions. Artifacts containing ferrous and nonferrous materials will degrade faster in aggressive environments like seawater than in less aggressive ambient conditions (Angelini, Grassini, and Tusa, 2013). XRD can be used to determine the types of minerals in artifacts and to conserve and inhibit degradation based on the type of metal, which can include copper and its alloys, iron and its alloys, and other metals (including silver, lead, and zinc) (Cano and Lafuente, 2013). Information about the crystal's morphology, elemental composition, and structure makes it possible to determine the constituents of the corrosion layer (Neff, Reguer, and Dillmann, 2013; Hamilton, 2010).

3.4. The XRF analysis of the surface corrosion of the iron cannonball material immersed in water

The results obtained from analyzing the surface corrosion of the iron cannonball material immersed in water using XRF are shown in Table 2.

Table 2 Characterization of surface corrosion using XRF

<table>
<thead>
<tr>
<th>No</th>
<th>Dry active corrosion</th>
<th>Wet active corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Element</td>
<td>Amount (%)</td>
</tr>
<tr>
<td>1</td>
<td>Cl</td>
<td>66.60</td>
</tr>
<tr>
<td>2</td>
<td>Fe</td>
<td>32.11</td>
</tr>
<tr>
<td>3</td>
<td>Ca</td>
<td>0.32</td>
</tr>
<tr>
<td>4</td>
<td>Mn</td>
<td>0.26</td>
</tr>
<tr>
<td>5</td>
<td>Al</td>
<td>0.15</td>
</tr>
<tr>
<td>6</td>
<td>SiO₂</td>
<td>0.20</td>
</tr>
<tr>
<td>7</td>
<td>S</td>
<td>0.064</td>
</tr>
<tr>
<td>8</td>
<td>P</td>
<td>0.039</td>
</tr>
<tr>
<td>9</td>
<td>Cd</td>
<td>0.011</td>
</tr>
<tr>
<td>10</td>
<td>Sb</td>
<td>0.0066</td>
</tr>
<tr>
<td>11</td>
<td>Sn</td>
<td>0.0041</td>
</tr>
</tbody>
</table>

Table 2 shows the XRF results of characterizing the corrosion of the iron cannonball underwater. Table 2 shows that chlorine is the most abundant element in corrosion products. Table 2 shows that the leading causes of the corrosion of the underwater cannonball culture remnants (submerged in seawater) are chloride ions.

3.5. SEM characterization of the surface corrosion of the iron cannonball material immersed in water

The SEM results of the characterization of the surface corrosion of the cannonball heritage material are shown in Figure 5. The cannonball contains hollow cavities, and the iron material is damaged, as shown in Figure 6.
Figure 5 SEM images of the cannonballs, as obtained with magnification at (a) 50x and (b) 350x

Figure 6 SEM images of the cannonballs at the point of rust growth, as obtained with magnifications of (a) 50x, (b) 350x and (c) 500x

3.6. Stabilizing/coating the iron cannonball underwater heritage material

The coating material used is a microcrystalline wax, and various concentrations of 5, 10, 20, and 50% wax were achieved with turpentine oil solvents. Coating materials, namely, carboxylic monoacids in an ethanol solution (Mohammed, De Keersmaecker, and Adriaens, 2016), acidic solutions from plants (Chellouli et al., 2016), and carboxylates, have been applied to iron-based objects by several researchers after the conservation process is completed to inhibit the corrosion process (Liu et al., 2018). Microcrystalline wax coats the iron metal that has finished passivation so that the metal is not prone to corrode again. The results of coating using microcrystalline wax can be seen in Figure 7.

Figure 7 Layered iron cannonball using microcrystalline wax with concentrations (a) 5, (b) 10, (c) 20, and (d) 50%
Figure 7 shows different colored iron cannonball materials coated with the microcrystalline solution. From the results of the image, the stabilization or coating of the iron cannonball material was achieved using a 5, 10, 20, and 50% microcrystalline wax solution. The results showed that the most suitable solution did not change the color of the sample, which was achieved by a microcrystalline wax solution with a concentration of 5%. In this study, the author uses 5% wax microcrystalline with solvent turpentine oil to coat the iron metal that has finished passivation so that the metal is not prone to further corrosion. The results of the analysis and XRF characterization of iron cannonball material objects lingering underwater before and after conservation can be seen in Table 3. The next step is cleaning with soapy water to remove any residual corrosion products. Soap is an alkaline salt of fatty acids and will thus partially be hydrolyzed by water. Therefore, the soap solution in water is alkaline.

\[
\text{CH}_3(\text{CH}_2)_{16}\text{COONa} + \text{H}_2\text{O} \rightarrow \text{CH}_3(\text{CH}_2)_{16}\text{COOH} + \text{OH}^- + \text{Na}^+
\]

**Table 3** XRF characterization of the corroded surface of the iron cannonball material before and after conservation

<table>
<thead>
<tr>
<th>No</th>
<th>Before conservation</th>
<th>After conservation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry active corrosion</td>
<td>Wet active corrosion</td>
</tr>
<tr>
<td>1</td>
<td>Cl 66.60</td>
<td>Cl 64.96</td>
</tr>
<tr>
<td>2</td>
<td>Fe 32.11</td>
<td>Fe 24.73</td>
</tr>
<tr>
<td>3</td>
<td>Ca 0.32</td>
<td>Mn 0.27</td>
</tr>
<tr>
<td>4</td>
<td>Mn 0.26</td>
<td>Al 0.10</td>
</tr>
<tr>
<td>5</td>
<td>Al 0.15</td>
<td>SiO$_2$ 0.20</td>
</tr>
<tr>
<td>6</td>
<td>SiO$_2$ 0.19</td>
<td>S 0.085</td>
</tr>
<tr>
<td>7</td>
<td>S 0.064</td>
<td>P 0.051</td>
</tr>
<tr>
<td>8</td>
<td>P 0.039</td>
<td>Cd 0.0092</td>
</tr>
<tr>
<td>9</td>
<td>Cd 0.011</td>
<td>Sb 0.0047</td>
</tr>
<tr>
<td>10</td>
<td>Sb 0.0066</td>
<td>Sn 0.0047</td>
</tr>
<tr>
<td>11</td>
<td>Sn 0.0041</td>
<td>- -</td>
</tr>
</tbody>
</table>

The weak base solution from soapy water can help clean surface corrosion products. The iron cannonball material was washed with soapy water and then washed with an aqueous kaffir lime extract (weak acid solution). Citric acid is a type of acid that is nontoxic, nonirritating, and environmentally friendly (Liu et al., 2018). Citric acid is also easy to find in citrus-like organic substances, including citrus (kaffir lime) and lemon (citrus lemon). The citric acid content contained in kaffir lime is 45.8 g/L, while the citric acid content contained in lemon is 48.0 g/L (Penniston et al., 2008). The aqueous kaffir lime extract contains citric acid and ascorbic acid, which are weak acids, and thus removes impurities on the surface of the ball cannon. Iron cannonball material was characterized using XRF before and after conservation (Table 3) and showed a significant difference between the data. From this, it can be concluded that the corrosion process on the object was lost and stopped.

4. Conclusions

The degree of weathering and corrosion can be classified in order by implementing four appropriate levels of active corrosion, namely, low, medium, high, and the next. XRD and XRF were used to analyze and characterize the corroded surface before conservation and showed the existence of an akageneite corrosion product, which is the most important
corrosion product of the iron material. Thus, chloride ions were present and were the cause of the corrosion of iron oxyhydroxides, which form chlorine (including akageneite). The deactivation or passivation using aqueous Na$_2$CO$_3$ 5% with a pH of 11-13 proved to be able to eliminate the concretion and prevent the corrosion of iron cannonball material objects lingering underwater. Stabilization with a coating of 5% wax microcrystalline with a solvent of turpentine oil was proven to coat and protect the cannonball from further corrosion without damaging the color and shape of the iron cannonball material, preserving the underwater heritage. Iron cannonball material after conservation is finished and stored in the museum, and future work is monitoring the material to ensure corrosion has stopped.

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