

# Conservation of underwater cannonball heritage obtained from a shipwreck in the sea of Batavia, Jakarta, Indonesia

Riyanto Riyanto (✉ [riyanto@uii.ac.id](mailto:riyanto@uii.ac.id))

Universitas Islam Indonesia <https://orcid.org/0000-0002-0946-7112>

**Imam Sahroni**

Universitas Islam Indonesia

**Muhammad Malthuf Jazuli**

Universitas Islam Indonesia

**M. Miqdam Musawwa**

Universitas Islam Indonesia

**Nahar Cahyandaru**

Universitas Borobudur

**Endang Tri Wahyuni**

Universitas Gadjah Mada

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## Research article

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# Abstract

The Borobudur Conservation Center in Magelang, Central Java, Indonesia has received underwater cannonballs from a shipwreck in the sea near Batavia, Jakarta, Indonesia. This artifact is a shipment from the Directorate for the Preservation of Cultural Heritage and the Indonesian Ministry of Education and Culture. This study aims to conserve the underwater cannonball before it is stored in a museum. The removal of 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. This research aims to stop the process of corrosion and conserve iron objects in aqueous alkali solutions, and the potential corrosion was measured. 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, which was 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, so this stage should solve the conservation problems associated with the object so that the objects 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 66.603% and 64.963%, 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 to conserve cultural heritage materials, including underwater iron cannonballs.

## 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 the cultural heritage, conservation actions are needed [1].

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 [1]. 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), of which there 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. Fig. 1 shows the geological location of the shipwreck materials, namely, iron cannonballs.

The underwater heritage of constituent materials also varies greatly, ranging from wood, metal, ceramics, and other materials. Underwater heritage has a significant value to history, culture, and science and can thus be defined as cultural heritage. Underwater heritage is meaningful to history, culture, and science and has thus been described as cultural heritage. The preservation of underwater cultural heritage is essential because of the high value of cultural heritage, which is generally in a condition that is already obsolete.

Economically, underwater relics are also high-value, and their protection is threatened [2].

Marine heritage conservation has its characteristics and degree of difficulty, which differ from the characteristics and difficulty of conserving cultural heritage in general. Underwater relics experience damage and weathering by chemical reactions that occur in the water and other factors, such as primary biological activity. The method used to conserve cultural reserve land cannot be directly applied to underwater cultural heritage. The conservation method used for underwater relics must pay attention to the characteristics of materials and weathering that occurs. Conserved underwater relics should also be handled by planning before the adoption, at the time of appointment, and during their 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 [3].

The most striking feature of the corrosion of iron in an underwater environment (sea) is the formation of a thick concretion. Concrete formed on the iron that was buried beneath the seafloor and exposed to seawater. Concrete created by the iron corrosion products interact with the material adjacent to the iron. Iron is not toxic, and biological organisms quickly attack iron materials that sink in seawater. These organisms build layers of bone material, mainly calcium carbonate ( $\text{CaCO}_3$ ). The further diffusion of iron II ions ( $\text{Fe}^{2+}$ ) and iron III ions ( $\text{Fe}^{3+}$ ) during iron corrosion change the underlying chemical nature of biological materials. In concretion,  $\text{Fe}^{2+}$  ions are swapped with calcium ions ( $\text{Ca}^{2+}$ ) to produce  $\text{CaCO}_3$  or iron carbonate ( $\text{FeCO}_3$ ) siderite. Some  $\text{CaCO}_3$  also interacts with hydrogen ions ( $\text{H}^+$ ) to form calcium bicarbonate [ $\text{Ca}(\text{HCO}_3)_2$ ], which increases the pH of the solution. Increasing the pH then causes the gradual settling of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , forming oxides, hydrated chloride oxides, and hydroxides. This process of filling the holes and pores in concretion forms a cement matrix of iron, which slowly dissolves and replaces the original matrix of calcite [2]. During crystallization, in areas with a low oxygen content, the reaction between the iron ions and sulfide ( $\text{S}^{2-}$ ) ions occurs due to the sulfate generated from the formation of iron (II) sulfide ( $\text{FeS}$ ) and the element sulfur [2].

## Research aim

This paper aims to conserve underwater cannonball heritage. The removal of the protective cover crust from iron artifacts without the correct and proper method can cause the artifact to rapidly corrode. To prevent damage, artifacts must be conserved in the right solution. This research aims

to stop the process of corrosion and conserve iron objects in aqueous alkali solutions, and the potential corrosion was measured.

## **Material And Methods**

### ***Identification of samples***

The object examined was the iron cannonball underwater cultural remnants taken from the sea of Batavia/Jayakarta, Indonesia (**Fig. 1**). The identified rates of weathering can be compared by paying attention to every object that is experiencing active corrosion, which is characterized by the emergence of new rust (such as the details of a fluid). Objects that are undergoing active corrosion can be grouped and sequenced by the implementation of appropriate levels of handling the active corrosion. The identification of the weathering of the underwater iron relics is observed.

### ***Analysis and characterization of the iron cannonball surface reveals an underwater culture***

The existing components in the sample were studied and characterized using X-ray diffraction (XRD), shimadzu X6000 at a voltage of 45 kV with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and portable Olympus X-ray fluorescence (XRF) systems, and the corrosion of the object surface was analyzed using a microscope (HMR) and a Jeol JSM-T300 scanning electron microscopy (SEM) system.

### ***Passivation/deactivation corrosion***

The iron cannonball material was immersed in a solution of 5% sodium carbonate (Fig. 2). The pH was maintained at the alkaline condition in the range of 11-13. If the pH goes down, then it should be raised in the field with a solution of sodium hydroxide. Soaking was performed about once a week, and the material was then rinsed with water and subsequently with 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.

### ***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. The microcrystalline wax solution was further mounted on the soft iron

cannonballs using a brush. The schematic experimental procedure used in this research is shown in **Fig. 3**.

## Results And Discussion

### *Identification of sample*

The weathering of the iron relics is observed underwater. The result of the identification of the sample is shown in **Fig. 4**. **Fig. 4** 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. Fig. 4a shows the iron metal that undergoes weathering and a low level of corrosion. Fig. 4b shows the iron metal that undergoes weathering and corrosion, and cracks are present on the ferrous objects. Fig. 4c shows the iron metal that undergoes weathering and corrosion, where large amounts of iron suffered from splitting. Fig. 3d shows iron metal that undergoes weathering and corrosion, exhibiting advanced damage, which gives rise to rupture and the destruction of the iron objects.

When iron is exposed to the atmosphere, the environment forms different iron-oxides, such as magnetite ( $\text{Fe}_3\text{O}_4$ ), hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) [3]. At temperatures higher than 560 °C, the general sequence of the iron-oxide layer (from the interior to each surface) is Fe/FeO/ $\text{Fe}_3\text{O}_4$ / $\text{Fe}_2\text{O}_3$ / $\text{O}_2$  [4]. The redness of the rust powder and the presence of many cracks and cavities on the surface of the object are indicative of an active corrosion process being in progress, causing the continuous loss of metals, as well as the degradation of the mechanical properties [5]. The corrosion of iron-based archeological artifacts immersed in seawater is an electrochemical process that involves anodic and cathodic reactions in an aqueous electrolyte environment, and biological processes also involve anaerobic bacteria [2]. When iron is put into solution, the oxide layer grows slowly, forming oxide compounds, such as goethite ( $\alpha\text{-FeOOH}$ ), akageneite ( $\beta\text{-FeOOH}$ ), and lepidocrocite ( $\gamma\text{-FeOOH}$ ) [3, 6, 7, 8, 9, 10, 11, 12].

### *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 **Fig. 5**. **Fig. 5** 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 **Fig. 5a** and wet active corrosion, as shown in **Fig. 5b**.

The ongoing problem with iron archeology is the continued corrosion that occurs after excavation, which is 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 [5]. The weathering of underwater relics generally takes place faster than that of 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

[1]. The speed of weathering is a result of the interaction of the material with water containing salt and exhibiting a biological activity. Chemical weathering reactions occur quickly in an aqueous medium because the reaction takes place effectively.

### ***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 **Fig. 6a and Fig. 6b**. 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 [13, 14, 15, 16, 17]. 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 [18].

The X-ray diffraction patterns in **Fig. 6** clearly show the distinction of the compounds contained in the corroded material. As shown in **Fig. 6a**, peaks are observed at  $2\theta$  positions of  $26.67^\circ$  and  $35.11^\circ$ , while **Fig. 6b** shows peaks at  $2\theta$  positions of  $26.67^\circ$  and  $35.17^\circ$ . These peaks correspond to akageneite, as supported by the research of Gil et al. [19], who found the presence of akageneite to correspond to the peaks at  $2\theta = 26.68^\circ$  and  $2\theta = 35.18^\circ$ . The X-ray diffraction results indicate that the sample obtained from the corroded iron contains two types of iron oxide, akageneite and lepidocrocite.

The dominant phases in the iron artifacts are goethite ( $\alpha\text{-FeOOH}$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). The presence of these material types in the corrosion products explains the good preservation of the base metal (iron) for centuries and the stability after excavation. The corrosion product of iron-containing chloride ions, for example, is akageneite [20]. 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 [5].

**Fig. 6** shows the X-ray diffraction results obtained for the iron cannonball sample corroded by wet corrosion, which was shown to form four types of iron oxide, i.e., halite ( $\text{NaCl}$ ), akageneite, briartite, an iron mineral that is a gray metallic opaque sulfide, namely,  $\text{Cu}_2(\text{Zn, Fe})\text{GeS}_4$ , and famatinite (copper, antimony, and sulfur), which is a pink-brown mineral containing copper, antimony, and sulfur.

Various artifacts found on the shipwreck, including small arms and ammunition, show their involvement in naval battles [21]. The results showed that the cannonball was made of iron and was produced with sand casting molds. The sand found in the cavities of the cannonballs were also studied by petrography [22]. 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

No.	Dry active corrosion		Wet active corrosion	
	Mineral	Amounts (%)	Mineral	Amounts (%)
1	Halite	9.12	Akageneite	96.68
2	Akageneite	89.63	Lepidocrocite	3.32
3	Famatinite	0.72	-	-
4	Briartite	0.53	-	-

The iron mineral is akageneite (III) oxide hydroxide/chloride, with the formula  $\text{Fe}^{3+}\text{O}(\text{OH}, \text{Cl})$ . However, lepidocrocite, also called esmeraldite or hydrohematite, is a natural occurring iron oxide-hydroxide mineral with the formula  $\gamma\text{-FeO}(\text{OH})$ . **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.

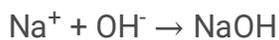
Artifacts containing ferrous and nonferrous materials, will degrade faster in aggressive environments, such as seawater, than in less aggressive ambient conditions[23]. XRD can be used to determine the types of minerals in artifacts and to conserve and inhibit degradation based on the type of metal, which can include copper and its alloys, iron and its alloys, and other metals (including silver, lead, and zinc) [24]. Information about the morphology, elemental composition, and structure of the crystal makes it possible to determine the constituents of the corrosion layer [25].

The reaction mechanism that occurs during underwater metal corrosion is as follows, according to Hamilton [1]:

Reactions that occur on an inert metal surface (cathode)



Hydroxide ions react with sodium ions in water



At the anode, the reaction produces iron ions



Fe reacts with chloride ions in salt-containing water (seawater)



Underwater conditions containing oxygen will continue to form hydroxides during the reaction:



The hydroxide compound formed in the oxygen-containing solution will experience a secondary reaction, and corrosion deposits will form around the metal surface of the anode:



Secondary reactions involving ferric ions produce other products during corrosion:



### ***The XRF analysis of the surface corrosion of the iron cannonball material immersed in water***

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

**Table 2**

Characterization of surface corrosion using XRF

No	Dry active corrosion		Wet active corrosion	
	Element	Amount (%)	Element	Amount (%)
1	Cl	66.603	Cl	64.963
2	Fe	32.105	Fe	24.730
3	Ca	0.320	-	-
4	Mn	0.259	Mn	0.265
5	Al	0.147	Al	0.095
6	SiO <sub>2</sub>	0.193	SiO <sub>2</sub>	0.195
7	S	0.064	S	0.085
8	P	0.039	P	0.051
9	Cd	0.011	Cd	0.0092
10	Sb	0.0066	Sb	0.0047
11	Sn	0.0041	Sn	0.0047

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

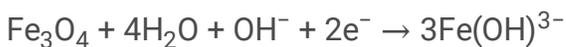
## ***SEM characterization of the surface corrosion of the iron cannonball material immersed in water***

The SEM results of the characterization of the surface corrosion of the cannonball heritage material is shown in **Fig. 7**. The cannonball contains hollow cavities, and the iron material is damaged, as shown in **Fig. 8**.

## ***Passivation/deactivation of the corroded cannonball heritage material***

Passivation prevents the corrosion of an object with a particular method. For the *passivation* method used in this study, the sample is soaked in a solution of 5% sodium carbonate. The pH is maintained between 11-13 using sodium hydroxide. If the pH goes down, then the pH should be increased within the range with a solution of sodium hydroxide, and then, the object should be rinsed with water and subsequently washed using distilled water. The purpose of drying is to see the corrosion development, and if corrosion still happens, then the corrosion process is repeated until corrosion stops. Soaking was conducted for five months, and a mixed solution was replaced after about four days to a week. Before the process, the cleanup crust or rust was not passivated. Layers of the coating would be a natural protector in the meantime. Next, manual cleanup was performed using tools such as brushes, a skavel, needles, a chisel, a hammer and other devices. The cleaning level is adjusted to the level of corrosion, and if the object is still obviously in poor condition, then the object will be made as clean as possible. If the form of the object is already less precise, then cleanup should be performed carefully so that the crust is not released. Not all of the surface should be clean, as to the form of the object should be maintained/found. If corrosion is already very advanced, and shapes are not visible at all, then mechanical cleaning is only performed on the surface.

Alkali solutions, such as sodium hydroxide and potassium hydroxide, will remove rust from iron and steel. Alkali solutions combined with sequestering agents, which are used to hold the dissolved iron in solution, can be very effective, particularly at near-boiling temperatures. Under the  $\text{Fe}_3\text{O}_4$  deposit, the following reactions can occur on the substrate:



Next, cleaning is performed, where the cleaning phase is the core of the conservation activities. Thus, cleaning should be completed to address the conservation problems of the object so that the object can last for a long time. Materials were processed by cleaning with soapy water, using washing fruit extract and kaffir lime water, and rinsing with distilled water. At the end of the flushing and drying stage, flushing is performed to completely remove the chloride solution. After the completion of the drying stage, rinsing is performed. The drying process is carried out by warming in the blazing sun and using a blow dryer.

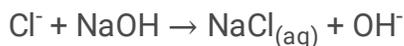
## ***Stabilizing/coating the iron cannonball underwater heritage material***

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 [26], acidic solutions from plants [27], and carboxylates, have been applied to iron-based objects by several researchers after the conservation process is completed to inhibit the corrosion process [28]. Microcrystalline wax is used to coat 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 **Fig. 9**. **Fig. 10** shows the iron cannonball that has been conserved and is ready to be sent to the museum.

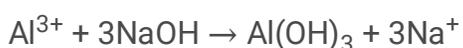
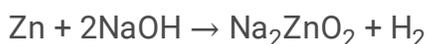
Fig. 11 shows some of the different colored iron cannonball materials coated with the microcrystalline solution. From the results of the image, the stabilization or coating of the iron cannonball material was achieved using a 5, 10, 20, and 50% microcrystalline wax solution. The results showed that the most suitable solution did not change the color of the sample, which was achieved by a microcrystalline wax solution with a concentration of 5%. The iron cannonball material is still prone to further corrosion after passivation. Therefore, stabilization/coating must be done as soon as possible. This stabilization stage is the last stage of the passivation process that was completed after all. In this study, the author uses 5% wax microcrystalline with a solvent turpentine oil to coat the iron metal that has finished passivation so that the metal is not prone to further corrosion.

**Fig. 11** shows a significant difference between the tangible cultural heritage of the cultural iron cannonball immersed in water before conservation (a) and after conservation (b). **Fig. 11** shows that the method of conservation used in this research is very suitable to be used in the conservation of iron material underwater. However, this conservation research is not ideal because the iron cannonball material used in the study existed for far too long on the mainland, this cultural heritage iron material should be directly conserved after the rapture of the deep sea. 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**.

**Table 3** shows that after conservation, elemental Cl and some metals have reacted with NaOH. Elemental Cl is the main element causing wet and dry corrosion. After immersion with 5% NaOH, the Cl element reacts with NaOH.



The artifact is soaked for one week in 5% NaOH, rinsed with distilled water, and then cleaned physically with a brush; if the corrosion has not stopped, the process of soaking was repeated until corrosion stops. After corrosion stops, the iron cannonball shape was refined. NaOH and the metal react according to the following example:





**Table 3.**

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

No	Before conservation				After conservation					
	Dry active corrosion		Wet active corrosion		Test 1		Test 2		Test 3	
	Element	Amount (%)	Element	Amount (%)	Element	Amount (%)	Element	Amount (%)	Element	Amount (%)
1	Cl	66.603	Cl	64.963	Fe	98.90	Fe	98.72	Fe	99.35
2	Fe	32.105	Fe	24.730	Co	0.40	Cu	0.45	Mn	0.44
3	Ca	0.320	Mn	0.265	Mn	0.31	Zn	0.37	Cu	0.12
4	Mn	0.259	Al	0.095	Cu	0.20	Mn	0.29	V	0.06
5	Al	0.147	SiO <sub>2</sub>	0.195	Zn	0.17	Ti	0.17	Ni	0.04
6	SiO <sub>2</sub>	0.193	S	0.085	-	-	-	-	-	-
7	S	0.064	P	0.051	-	-	-	-	-	-
8	P	0.039	Cd	0.0092	-	-	-	-	-	-
9	Cd	0.011	Sb	0.0047	-	-	-	-	-	-
10	Sb	0.0066	Sn	0.0047	-	-	-	-	-	-
11	Sn	0.0041	-	-	-	-	-	-	-	-

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.



The weak base solution obtained 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 [29]. 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 [30]. 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.

The characterization of the iron cannonball material was performed using XRF before and after conservation (**Table 3**) and showed a significant difference between the data. The object undergoing active wet corrosion and drying before conservation showed the presence of chlorine, which is the result of the corrosion of the iron material, whereas on the object after conservation, the test results showed very significant differences, in which chlorine was no longer detected. From this, it can be concluded that the process of corrosion on the object was lost and stopped.

## Conclusion

The degree of weathering and corrosion can be classified in order by the implementation of 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<sub>2</sub>CO<sub>3</sub> 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.

## Abbreviations

XRD: X-ray diffraction; XRF: X-ray fluorescence; SEM: Scanning electron microscopy; EDX/EDS: Energy Dispersive X-Ray Spectroscopy; NaOH: Sodium hydroxide; Cl: Chlorine; Fe: Iron, Na<sub>2</sub>CO<sub>3</sub>: sodium carbonate.

## Declarations

### Availability of data and materials

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

### Competing Interest

The authors declare no competing interests.

### Author Contributions:

R and I.S contributed to the design and conception, drafting the article, and the final approval of the article. M.M.J, M.M.M, and N.C contributed to collecting the references, drafting the article, preparing all the figures and all tables, and the discussion. E.T.W contributed to the data analysis and discussion.

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## Figures



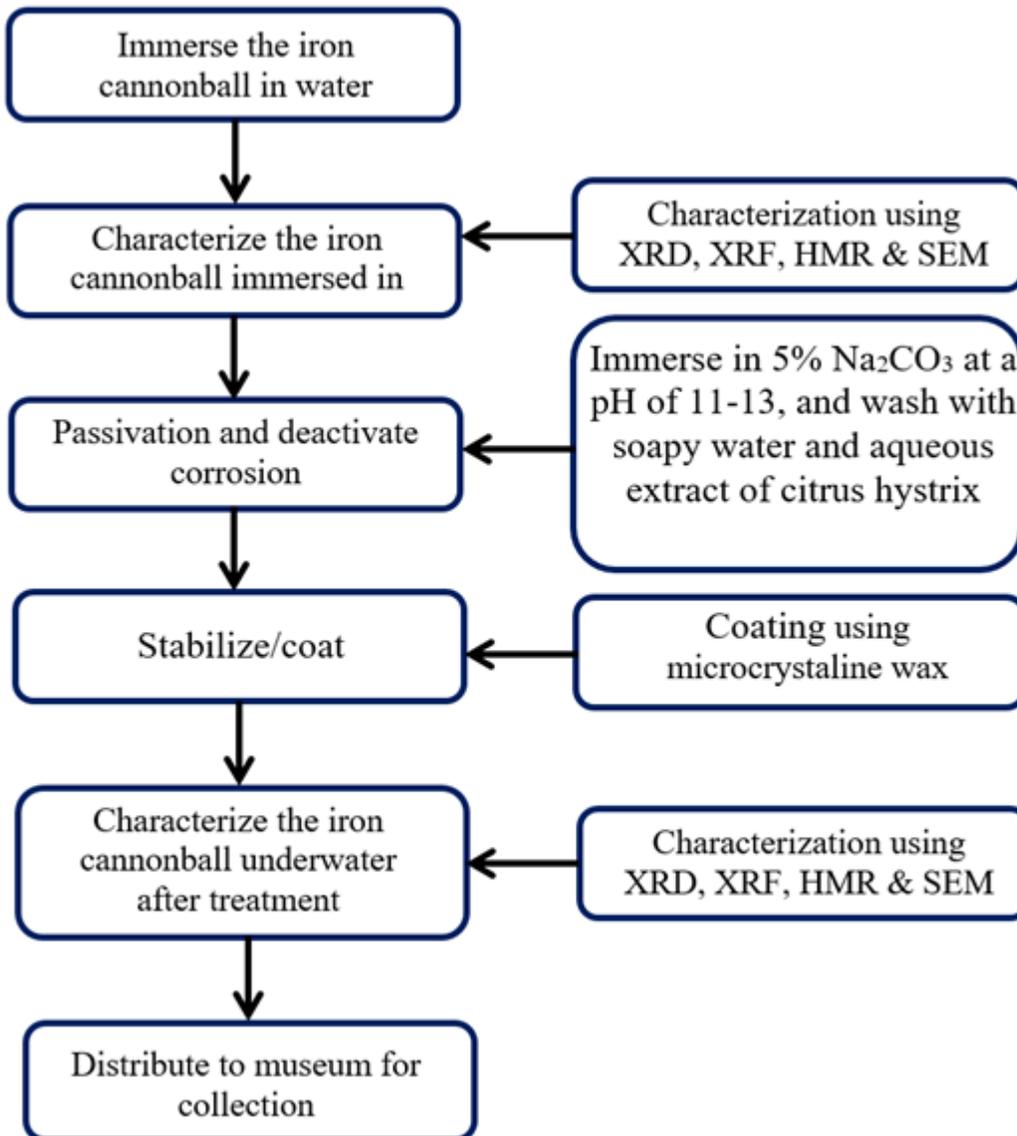
Figure 1

Geological location of the iron cannonball shipwreck materials



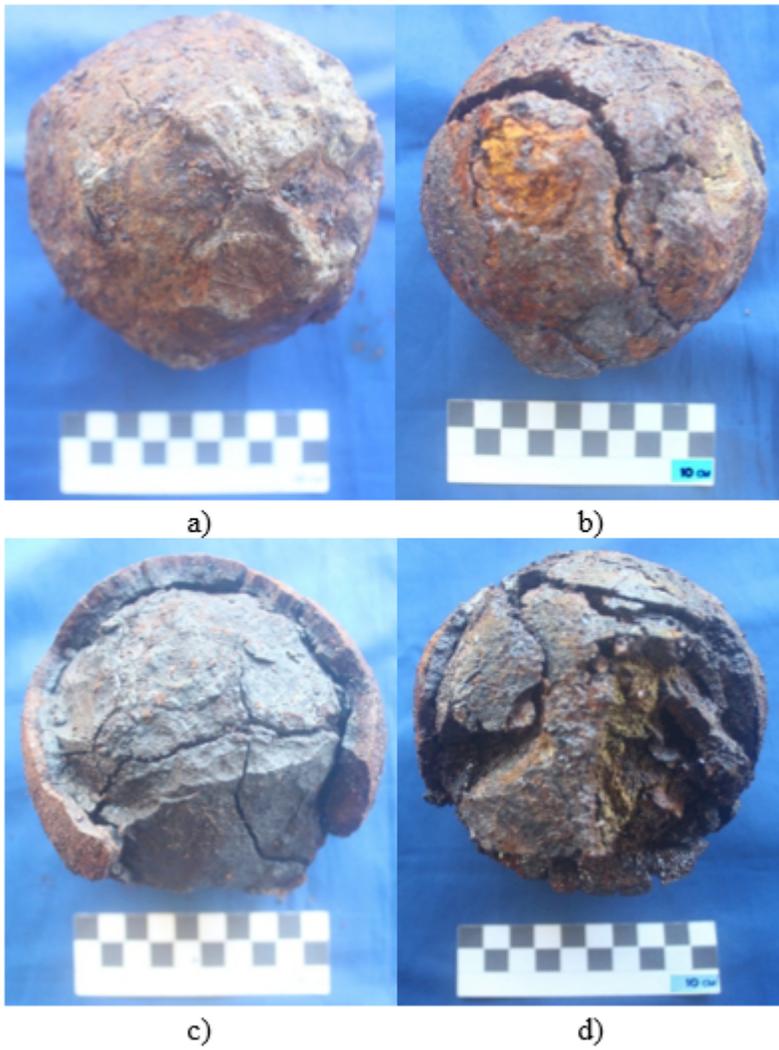
Figure 2

The iron cannonball material immersed in a solution of 5% sodium carbonate for one week



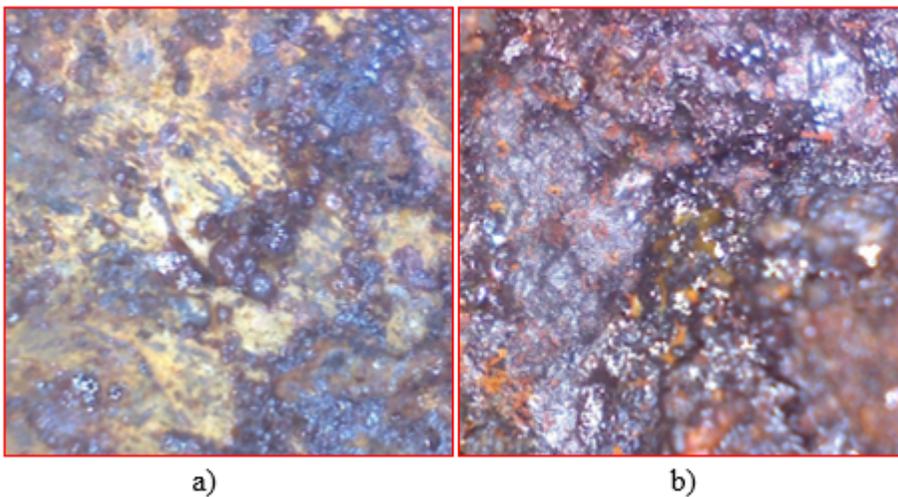
**Figure 3**

Schematic of the procedure used to conserve the cannonball underwater heritage



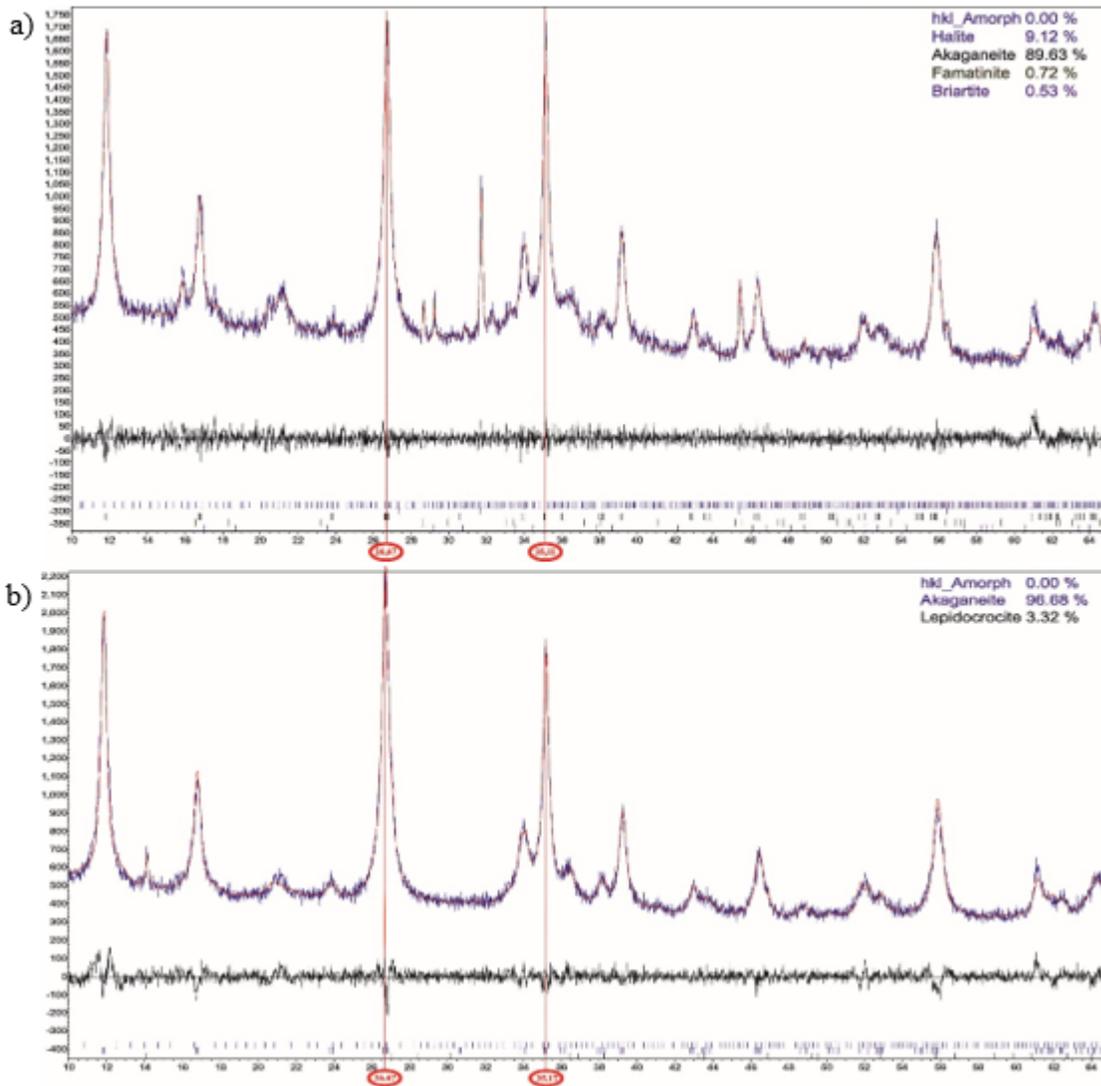
**Figure 4**

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



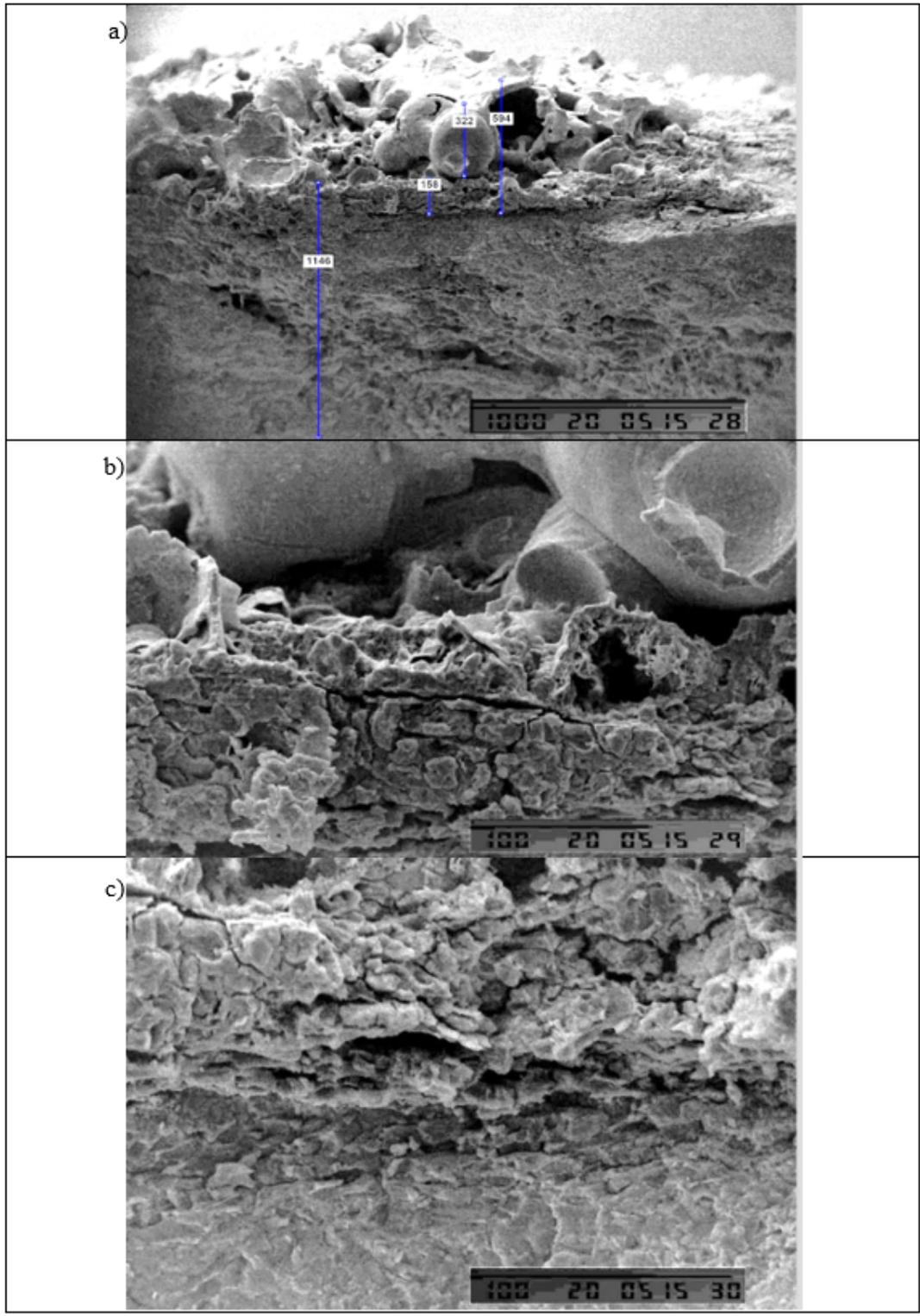
**Figure 5**

Handy microscope images, showing the corrosion of the iron cannonball material by (a) dry active corrosion and (b) wet active corrosion



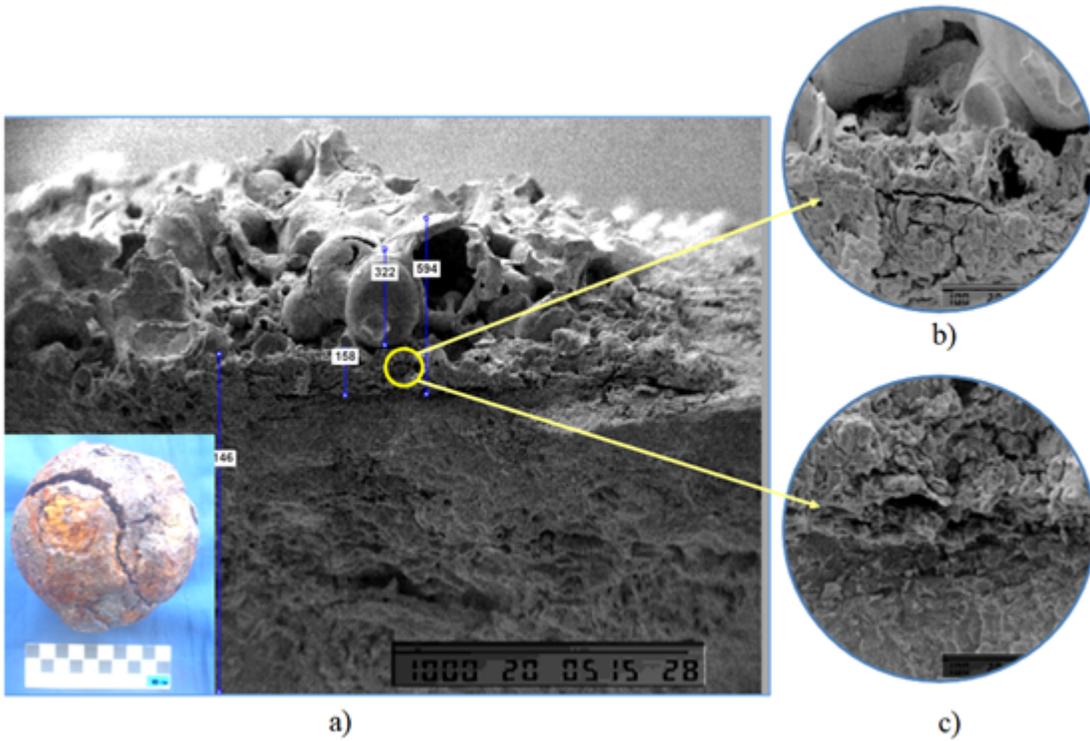
**Figure 6**

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



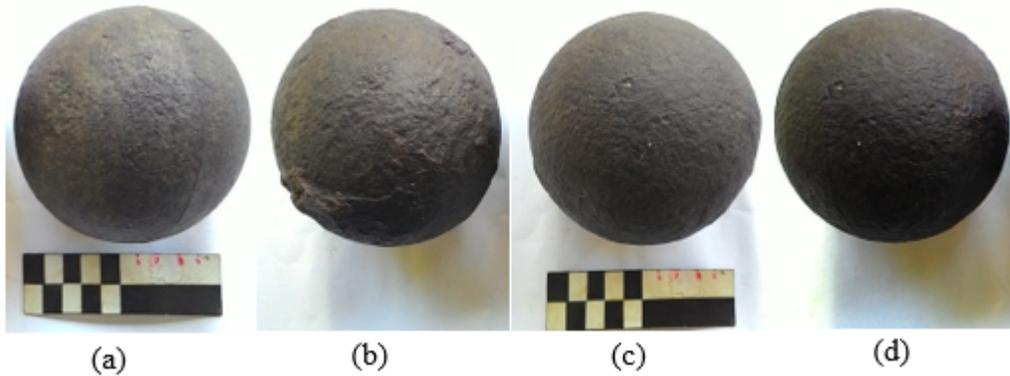
**Figure 7**

SEM images of the cannonballs, as obtained with magnification at (a) 50x (b) 350x and (c), 500x



**Figure 8**

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



**Figure 9**

Layered iron cannonball using microcrystalline wax with concentrations (a) 5 (b) 10 (c) 20 and (d) 50%



**Figure 10**

The iron cannonball has been conserved and is ready to be sent to the museum



**Figure 11**

Cannonballs (a) before and (b) after conservation