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Studying the Pathology and Corrosion of Two Iron Bayonet Belonging to the Persian Gulf Anthropology Museum, Iran

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Abstract

Hormozgan Province is one of the important historical areas in South of Iran. In this ancient area many significant objects have been obtained such as graffito pottery, Celadon, Sasanian coins, and iron weapons. Among other objects of this ancient area, two iron bayonets belonging to the first millennium to seven hundred BC that are protected in Persian Gulf Museum. The damages and corrosions observed on the surface of these artifacts have led to the destruction of the blades of these bayonets. The main objective of present study is identifying the type of corrosions and damages that have destructed these artifacts. In the same vein, in order to investigate the metal core, X-ray Radiography device has been deployed. In order to identify the type of corrosion products, XRD analysis and in order to analyze the types of corrosions on the surface and matrix of the artifacts, SEM-EDX and metallography device have been utilized. The obtained results indicated the existence of ferric chloride corrosion including Akaganéite (β-FeOOH) and Lorensite FeCl2 which indicate the intensity of corrosion and delamination metal matrix. Corrosion layer of Goethite (γ-FeOOH) were also recognized at the level of the objects.

Keywords: Persian Gulf, iron bayonets, SEM-EDX, XRD, Akaganéite, Lorensite

1. Introduction

The conducted investigations indicate that culture of Iron Age has expanded from Tigris, Mesopotamia and Soozianaplain (Ilam and Khuzestan plain) to the Far East. The discovery of this element is of a great importance after bronze and copper (Ansari, 2007, 52). This significant period in the archeology of Iran includes the time period of 500-1500 BC (the emergence of Achaemenid Empire). The classification of this long period of time includes Iron Age I (1500-1200 BC), Iron Age II (1200-800 BC), and Iron Age III (800-550 BC) and the last and the fourth Iron Age belongs to the Anthropology Museum of Persian Gulf and due to the fact that these objects are detained, their age, place of construction, and the place of discovery are not precisely known. These bayonets were made of iron and they were generally used for military purposes. These artifacts were detained by police in the Shahid Rajaei Customs Port and were delivered to cultural heritage organization of the Hormozgan Province. These artifacts are currently kept at Anthropology Museum of Persian Gulf. There are numerous damages on the surfaces of these bayonets which are caused by the placement of these bayonets in their burial environment. Numerous studies have been conducted on iron artifacts and their damages in the burial environment (Reguer and et al 2007). The most significant damages causing the destruction of the artifacts in their burial environment is the existence of chloride ions which create the corrosion product, which is named, Akaganéite (β-FeOOH) whose conditions and the way of formation is described (Reguer et al, 2007,PP2726-2744). The type of damaging corrosions on the iron artifacts and their morphology are stated in the article (Santareni, 2007, pp18-30).

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Morphology and the damaging layers and the corrosions, which are formed on the surface of these artifacts and finally led to the destruction and damage of these objects, are identified using electrochemical methods (Neff et al, 2007, pp 40-76). Considering the lack of attention and obsolescence which causes more damages to these unique artifacts, the present study aims at studying the corrosions and damages that have affected these artifacts in the burial environment and which gradually lead to the destruction of the bayonets.

2. Introducing the artifacts

2.1. Object number 1

Bayonet number one includes the handle part (hollow), blade and the tip of the bayonet. (Figures 1and 2). The protruded middle line has derived from the handle up to the middle of the blade. The length of the object is 26.50 cm, and the width is 6.50 cm, the diameter of the handle is 1.4 cm, the tip is 0.8 cm, and the weight is 124.89 grams. The bayonet is simple and has no specific decorations. Its surface is covered with hard mineral deposits and red- and yellow-colored products. In this object, the edges of the blade are intensely affected by the corrosion and some parts of the edges have been completely destructed.

2.2. Object number 2

This Bayonet includes the handle part (hollow), blade and the tip of the bayonet. (Figures 3 and 4). The protruded middle line extends from the handle up to the middle of the blade. The length of the bayonet is 19.56 cm, the width is 6.3 cm, the diameter of the handle is 1.6 cm, the tip's width is 0.5 cm, and the weight is 127.12 grams. Like, the first one, this bayonet is also simple and has no specific decorations observable in the radiographic images. This bayonet is also covered with hard mineral deposits and red-, yellow-, and brown colored products. The corrosion is intense in the edges and has led to the destruction of the edges of the blades of this bayonet.

Figure (1): The top view of object 1-Figure (2): The bottom view of object 1-Figure (3): The top view of object 2 -Figure (4): The bottom view of object 2

Considering the fact that these objects are detained, and similar bayonets have been discovered with different forms in Marlik, Deylaman, Talesh, Khurvin and Silk B cemeteries and possibly they are related to west region. According to the conducted investigations, bayonet number oneis probably related to the second millennium and the early first millennium BC and bayonet number 2 is related to the time interval of 700 to 1000 BC (Talaii, 1995).

3. Methodology

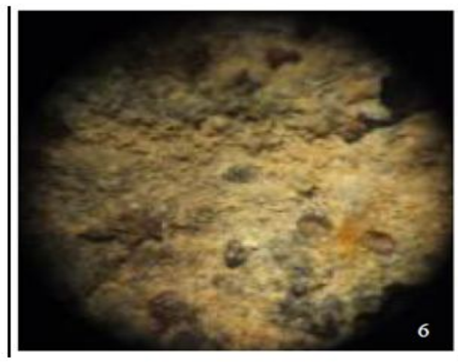
For elemental analysis and structural identification, scanning electron microscope (SEM), VEGALL model made by PESCAL Company of Czech Republic along with Energy-dispersive X-ray spectroscopy (EDS) RONTEC model made by Germany and the Software of QUALTAX model QX2 with amperage of 600MA and Voltage 1500 KV in Razi Metallurgical Research Center were utilized. For identifying the type of corrosion products, the XRD device (dispersive X-ray method) model T2T which belonged to SIEFERT Company were used with the amperage30 MA and Voltage of 40 KV in the Maintenance and Restoration Research Center. X-rayimages with the purpose of pathology and the corrosion infiltration were prepared in radiography laboratory of Amir-Al Momenin hospital in Zabol. Spot Test and pH meters and metallography were performed with the purpose of analyzing the objects' structure, the environmental features and damaging anions on the intended artifacts in the chemistry laboratory of Zabol Science faculty.

4. Results

Metals and alloys are crystal solids, meaning that, the metal atoms are placed in determined networks and consequently metal solids are produced as a result of their reoccurrences. The metals and alloys, in environmental conditions especially burial conditions, seek to return to their stable circumstances. In this regard, the more energy used for extracting the intended metal from the relevant ores, naturally, the metal has more tendency to return to its primary form. Hence, in burial conditions, the metals can return to their primary forms, in case the required conditions are prepared. This return will cause intense corrosions on the surface of the metal (Vatandoust,2012). Considering the contaminants or mineral deposits that are strictly adhered to the artifacts, the scalpel was used to take samples of different points.

Figure 5: Yellow-colored and furuncles corrosions on the surface of object number 2 with magnification of 40 x.

Figure 6: Dust and minerals deposits on the surface of object number 1 with magnification of 40 x.



4.1. Analyzing the surface deposits of artifact using Spot Test analysis

For analyzing the environmental features of the artifact in the burial environment and for the damaging anions which gradually lead to damage, corrosion, and finally providing the suitable circumstances for corrosion activities, this analysis was conducted on deposits which were on the artifacts. The results of these analyses are presented in Table 1.

Table 1: The obtained results from Spot Tests pf identifying the environmentally damaging anions

Objects	Fe^{3+}	NO_3^-	CO_3^{2-}	PO_4^{3-}	SO_4^{2-}	Cl^-
Object 1	+	-	+	-	+	+
Object 2	+	-	+	-	+	+

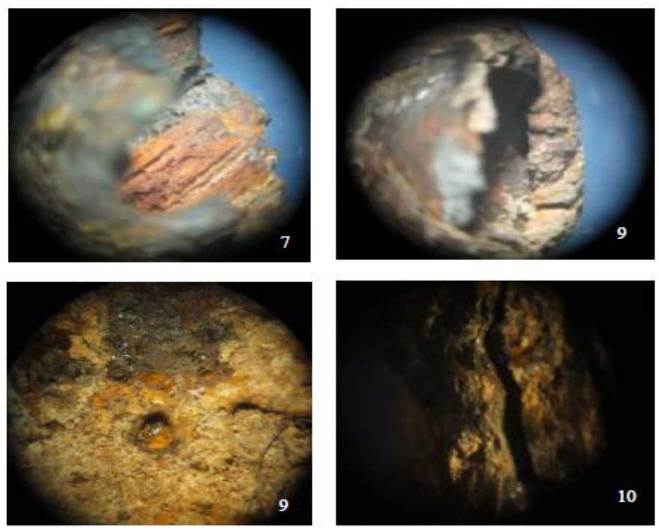
The conditions of the objects are analyzed using the pH test meters and the pH was determinedto be 5.5 (Asola, 1997).

4.2. Microscopic analyses

The bayonets, considering their application, had been placed on a wooden handle. According to Figures 7-8 which are taken from the inner holes of the handles, the devastating effect of iron on organic materials have been recognized. Due to the corrosions of iron, the cellulose fibers can be decomposed and have gradually decomposed the woods that were once in the handles (Scott, 2009, p.150). The remaining wood shave turned to fibers in the handle of object 1 which is due to the decomposition of cellulose by iron rust. Another damage that has intensely devastated the surfaces of these artifacts and has led to the distortion of the surface is pitting corrosion. This kind of corrosion is highly positional and causes the pitting and perforation of the artifacts ‘surfaces. This kind of corrosion occurs in places that have anion Cl-, this corrosion is regarded as the worst kind of corrosion which can be observed in all the surface of the two bayonets (Figures9 and 6). The growth of these pits is in the direction of gravity force. The other kind of corrosion which can be observed in these artifacts is separated in layers and leads to the fraction of a piece of the artifact are corrosion with the tension.

In some parts of the handle, these layers are separated easily (Figure 10). In Figures 13-16 the metallography of these type of fractures and laminated structure of the metal can be observed. Among the layers, red corrosion products are observable which will lead to the separation of the layers with a slight pressure. Among other damages of these objects, the Weeping Iron event can be mentioned (Scott, 2009, p.70). This damage is observed in the form of a series of brown-red furuncles on the surface of the artifact. One of the reasons of this damage might be the inappropriateness of relative humidity of the reservoir. The existing chloride ions with the reservoir's humidity will intensify the corrosion of these artifacts. Inclusions and hydrogen blisters are among other damages which lead to the destruction of the artifact's surface.

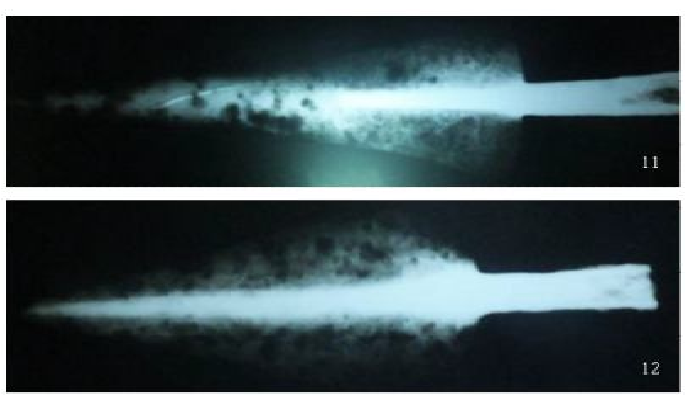
Figure 7- the remaining wood of the handle in object number 1 with the magnification of 40x, Figure 8- the remaining wood of the handle in object number 2 with the magnification of 40x, Figure 9- the pitting corrosion in object number 1 with the magnification of 40x, Figure 10- the tension corrosion in object number 2 with the magnification of 40x



4.3. The radiography analyses (X-ray)

The X-ray radiography was prepared with the purpose of pathology and technique identification of the work, and presents information such as construction method, decoration performance, connections types and … (Stuart, 2007). In order to identify the construction technique of the artifact and the infiltration rate of the corrosions, the radiography device was utilized. The radiography images indicated a little metal core in the middle-parts of the bayonets. But the intensity of the corrosions were very intense in the edges of object number 1 and will lead to the destruction and uneven state of the edges and is a sign of the corrosion intensity in the edges parts of the artifacts. The existence of some black-colored pits indicates the pitting corrosion in both cases (Figures 11 and 12). In the blades and edges, due to the lack of metal core and the corrosion intensity, the edges are fragile and brittle. The cracks and the tiny cracks are hidden under a bulk of iron corrosion products.

Figure 11: The radiography image of iron object number 1, Figure 12: The radiography image of iron object number 2

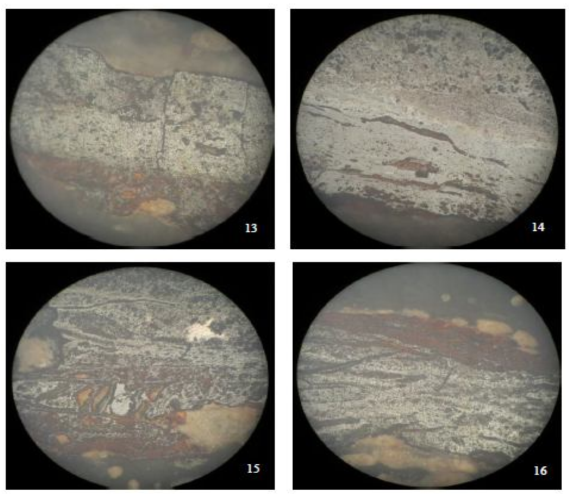


Likewise, in the radiography images, the integrity of the object is recognized and no joint points were witnessed in it. The object under study did not have the necessary metal core hence;metallography was conducted with the purpose of investigating the corrosion in the artifacts under study.

4.4. Metallography analyses

After taking the samples from the scalpel and preparing them, they were analyzed using metallography microscope. In the outer part of the handle section of object number 1, red colored corrosions and mineral material could be observed. According to the results of XRD analysis, the corrosions were of the types Fe_2O_3 ،γ-FeOOHand$FeCl_2$. The existence of cracks and fractions under the corrosion layer in object number 1 (figures 13-14). In figure 15, the outer part is seen as layered, among the layers, the corrosion products are of Hematite and Goethite. In the figure, the heterogeneity of the layers can be observed and different phases of metal and corrosion products of α-Fe_2O_3 ،β-FeOOH،$FeCl_2$, and mineral material are located besides each other with clear bordering. On the upper right side of the image, intact metal core (α-Fe) exists. Metallography image 16 displays the corrosion products and heterogeneity of the layers.

Figure 13- Metallography image of the handle of object number 1 with magnification of 250x, Figure 14- Metallography image of the blade of object number 1 with magnification of 250x, Figure15Metallography image of the handle of object number 2 with magnification of 250x, Figure 16- Metallography image of the blade of object number 2 with magnification of 250x



4.5. XRD device analysis

XRD device is a device analysis system that is utilized in determining the phases in samples such as soil, concrete, clay, alloys, and corrosion products (Stuart, 2007). Diagrams 1 and 2 are information that this device has given us regarding the corrosion products of the object under investigation which are presented in Table 2.

Diagram 1: XRD of Object number 1

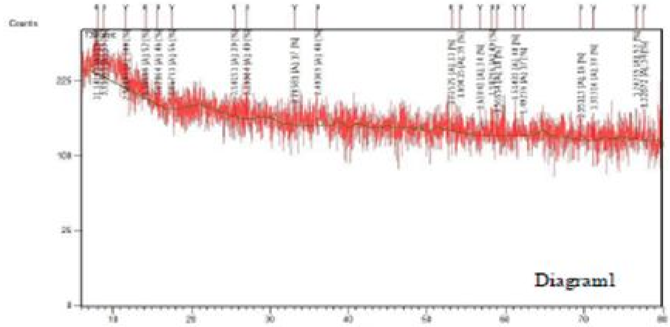


Diagram 2: XRD of Object number 2

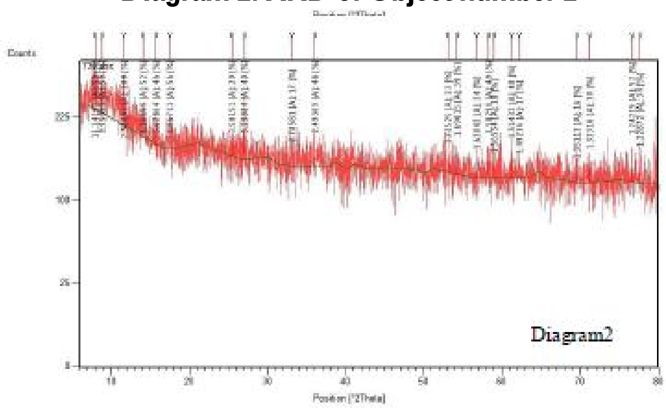


Table 2- The XRD results from samples

Results Obtained from XRD	Iron objects
$FeCl_2$, Clay Minerals, α-Fe_2O_3, γ-FeOOH	Object 1
$FeCl_2$, Clay Minerals, α-Fe_2O_3, β-FeOOH	Object 2

4.6. Structural study and analysis of the objects by using Scanning Electron Microscope device (SEM-EDX)

This method is used for elemental analysis in half-quantitative way. The purpose of this kind of analysis is determining the type of elements and their composition percentage in the intended objects. In all the images (17-18-19-20) heterogeneity can be observed in the analyzed samples. The existence of minerals and corrosion phases in figures 18-20 indicate the separation of the layers. Different phases (in images 19-20) among the layers DPL(Dense product layer)and TM(Transformed Medium)(Neff et al.2007, 45)are placed with pale and dark grey tonalities. The existence of pits and Inclusions can be observed in the images. The results of EDS half quantitative analysis of body of object number 1 (Table 3) and Object number 2 (Table 4) are dips.

Figure 17- SEM-EDX image of body of Object 2, with magnification of 500μm, Figure 18-SEM-EDX analysis of points on body of Object 2, with magnification of 50μm, Figure 19: SEMEDX image of body of Object 2, with magnification of 500μm, Figure 20- SEM-EDX analysis of points on body of Object 2, with magnification of 50μm.

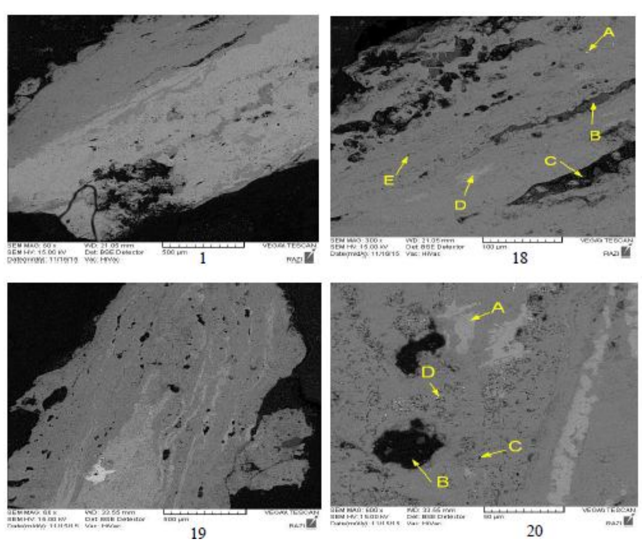


Table 3- the EDX analysis associated with the body of object 1

EDX	Fe	O	Ca	C	S	Si	Na	Cl	K
A	100/0	-	-	-	-	-	-	-	-
B	-	41/64	-	-	-	-	-	-	57/40
C	18/73	28/40	6/55	27/16	3/55	2/76	1/90	1/50	-
D	63/13	32/93	-	-	-	-	-	-	-
E	58/79	51.22	-	-	-	-	-	-	-

Table 4- the EDX analysis associated with the body of object 2

EDX	Fe	O	Ca	C	S	Si	Na	Cl	K
A	71/30	29/20	-	-	-	-	-	-	-
B	26/51	28/00	-	38/32	0/28	0/45	-	0/81	0/71
C	50/60	36/28	-	7/50	-	-	-	-	-
D	100/0	-	-	-	-	-	-	-	-

Considering the analysis of the points on body of object 1 in point A, pure iron in the form of α-Fe was witnessed; point B includes mineral materials, E and X include corrosion phases, and Dincludes corrosion of type γ-FeOOH. In the body of object 2, in Point D there is pure iron phase of α-Fe, point C iron corrosion, and in Point A goethite is analyzed. High percentage of carbon in the pits is probably because of the coals in the transformation of the ore.

5. Conclusion

Considering the analysis of the environmental conditions and the burial of the bayonets, the results of XRD indicates that the environmental conditions include chloride salts which directly influence the demolition of these artifacts especially at the edges of the blade, as determined by the X-ray analysis. The effect of chlorine ions on these bayonets have been analyzed in the form of corrosion products of Akaganéite β-FeOOH and Lorne site $FeCl2$. Moreover, the goethite corrosion γ-FeOOH is thermodynamically in the stable acidic and alkaline circumstances which exist in these artifacts. The SEM-EDX images indicate a kind of heterogeneity in the matrix of metals which depend on the construction conditions and in some points they are observed as being layered. The placements of these bayonets in the burial environment and the corrosions among the layers have caused separation among them which are also indicated in themetallography images.

6. Acknowledgment

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