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Conservation and Restoration of the Iron Artifacts excavated from the Late Ming Battleground Site in the Min River at Jiangkou Town, Pengshan District, Sichuan Province

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Abstract

This paper reports the conservation and restoration of 100 iron objects unearthed from the Jiangkou late Ming Battleground Site, including swords, spears, arrowheads, axes, and other implements. The investigation focused on the condition of the assemblage, the nature of its corrosion products, and the treatments required for stabilization. The objects display diverse forms of deterioration, notably mineralization, compact surface attachments, pitting, laminar exfoliation, cracking, fragmentation, and deformation. Portable X-ray fluorescence (p-XRF) and X-ray diffraction (XRD) were used to examine elemental composition and identify corrosion phases. Iron (Fe) was the dominant detected element, together with smaller quantities of Si, Al, P, S, Ti, As, and other trace elements. Goethite (α -FeO (OH)) and magnetite (Fe_3O_4) were the principal corrosion products, while quartz (SiO_2) and cementite (Fe_3C) occurred in several samples. These findings informed a coordinated conservation procedure that included condition documentation, removal of surface attachments, mechanical and chemical rust reduction, controlled drying, tannic-acid inhibition, structural consolidation, repair of damage, and application of a Paraloid B-72 protective coating. The treatment removed harmful corrosion and firmly attachments on the objects' surface, improved the physical stability of the objects, and strengthened prospects for their long-term preservation. The work also offers a practical reference for conserving iron objects excavated from river environments.

Key Words

Jiangkou, late Ming Battleground Site, iron artifacts, conservation and restoration, portable X-ray fluorescence, X-ray diffraction

Introduction

The Jiangkou late Ming Battleground Site lies in the channel of the Min River at Jiangkou Town, Pengshan District, Meishan City, Sichuan Province, China. It is situated approximately 60 km south of Chengdu and 20 km north of central Meishan.¹ After dividing at the Dujiangyan Irrigation System, the main stream of the Min River crosses the Chengdu Plain and reconverges near the site. All of the objects considered here were excavated from the Min River at Jiangkou and are mainly

weapons, especially iron sabres, arrowheads, and spearheads. Despite widespread mineralization, surface attachment, and laminar exfoliation, much of the assemblage retains a comparatively good state of preservation. Its long residence in a water-saturated riverbed nevertheless produced extensive corrosion, mineralized surfaces, adhering sand and gravel, and localized deformation.²

Before treatment began, the entire assemblage underwent a structured preliminary examination. For each object, provenance information was checked, visible deterioration

was recorded systematically, and previous conservation documentation was reviewed. A detailed condition assessment was then carried out to establish the degree of preservation, structural soundness, and overall completeness of the collection.

1. Deterioration Characteristics of the Excavated Iron Artifacts

The found iron objects consist of iron-carbon alloys with iron as the main element. They are easily corroded because of the activity of iron, the presence of pores and passages in the metal and the formation of electrochemical cells owing to the difference in the surface structure.^{3,4} The iron articles from Jiangkou have been buried in the Min River for a long time and therefore corroded before extraction. Being taken out of the burying environment does not always prevent this process; on the contrary, exposure to the new air may

accelerate the decay.^{5,6} A long-term underwater burial has led to the formation of tough and compact iron-oxide crusts which firmly adhere to different surfaces and are difficult to remove. In addition, some objects have lost their materials or been damaged mechanically. After the excavation, improper storage such as changes in temperature, humidity and air pollutants may cause further alterations or worsen the existing damage. According to the rate of deterioration and its effect on the stability of the artifacts, the observed phenomena can be divided into three types: stable, active and possibly reactivated deterioration^{11,16,17} (table 1). Stable deterioration indicates the destruction which has already taken place but is no longer developing or affecting the structural condition of the object. Active deterioration continues to deteriorate and endangers the conservation of the object. Possibly reactivated deterioration might begin again if the external conditions change, for example, because of the variation in the storage environment, resulting in renewed damage or the initiation of secondary corrosion processes.

Table 1 Classification of Deterioration in Iron Artifacts

No.	Type	Deterioration Type	Deterioration		
			Stable	Active	Potentially Activated
1	Iron	damage	√		√
2	Iron	Fracture	√		√
3	Iron	Cracking		√	√
4	Iron	Deformation	√		
5	Iron	Laminar Accretions		√	√
6	Iron	Pitting		√	√
7	Iron	Surface attachments		√	√
8	Iron	Mineralization		√	√
9	Iron	Pitting Corrosion		√	√
10	Iron	Microbial Deterioration		√	√

Investigation revealed that the majority of the objects were covered by much sand, gravel, corrosion products and other superficial substances. Although cleaned at first, there still existed a large amount of hard corrosion, pebbles and firmly adhered residues. Fracture, layering separation, surface destruction, mineralization and deformation were also found frequently. According to the present state of the whole assemblage and the conditions of its burial and storage, it is necessary to carry out conservation in time to prevent further degradation and ensure the long-term preservation.

2. Scientific analysis

Twelve items were selected for the study of corrosion in the Jiangkou assemblage. The selection was based on the principle of minimizing disturbance to prevent damage to the relics. The sample information is shown in table 2. Portable X-ray fluorescence (p-XRF) was used to determine the elemental composition, while X-ray diffraction (XRD) was employed to identify the corrosion products. Portable X-ray fluorescence spectroscopy is frequently applied in archaeo-

Table 2 X-ray Fluorescence (XRF) Analysis of the Elemental Composition of Iron Artifacts Excavated from the Jiangkou Late Ming Battleground Site (wt %)

No.	Artifacts No.	Artifact Type	Elements						
			Fe	Si	P	Al	S	Ti	As
1	2017PJIT2019: 6	Iron knife	71.2	13.9	0.16	14.6	/	/	/
2	2017PJIT2019: 9	Iron knife	87.4	4.55	0.55	6.67	0.46	/	/
3	2017PJIT2120: 8	Iron spearhead	95.3	2.51	0.38	1.49	/	/	0.28
4	2017PJIT1918: 4	Iron knife	88.1	6.06	0.08	5.57	/	/	/
5	2017PJIT2019: 19	Iron knife	86.8	1.39	0.14	1.55	9.88	/	/
6	2017PJIT2725: 80	Iron arrowhead	72.1	16.9	0.21	9.85	0.04	0.52	/
7	2017PJIT2725: 85	Iron object	73.6	15.5	0.04	10.4	0.04	0.47	/
8	2017PJIT2725: 86	Iron object	80.9	10.2	0.15	8.51	/	0.22	/
9	2017PJIT1919: 29	Iron spearhead	88.6	4.80	0.23	5.03	1.29	/	/
10	2017PJIT2725: 90	Iron object	91.2	1.73	1.73	4.15	1.17	/	/
11	2017PJIT2724: 45	Iron knife	67.6	14.3	0.89	14	0.24	/	/
12	2017PJIT2019: 24	Iron object	75.9	12.3	0.14	11.1	0.08	0.32	/
13	2017PJIT2120: 14	Iron knife	84.6	3.58	0.06	3.59	8.14	/	/
14	2017PJIT2019: 34	Iron dagger	91.2	5.12	/	3.7	/	/	/
15	2017PJIT2118: 188	Iron fork	88.1	5.31	/	6.54	/	/	0.04
16	2017PJIT2019: 37	Iron object	87.8	6.47	0.44	4.92	/	/	0.21
17	2017PJIT2119: 16	Iron knife	94.9	3.33	0.068	1.57	/	/	0.05
18	2017PJIT2119: 26	Iron knife	94.7	2.86	0.22	1.58	0.85	/	/
19	2017PJIT2020: 6	Iron knife	71.4	14	0.15	13.8	0.16	0.36	/

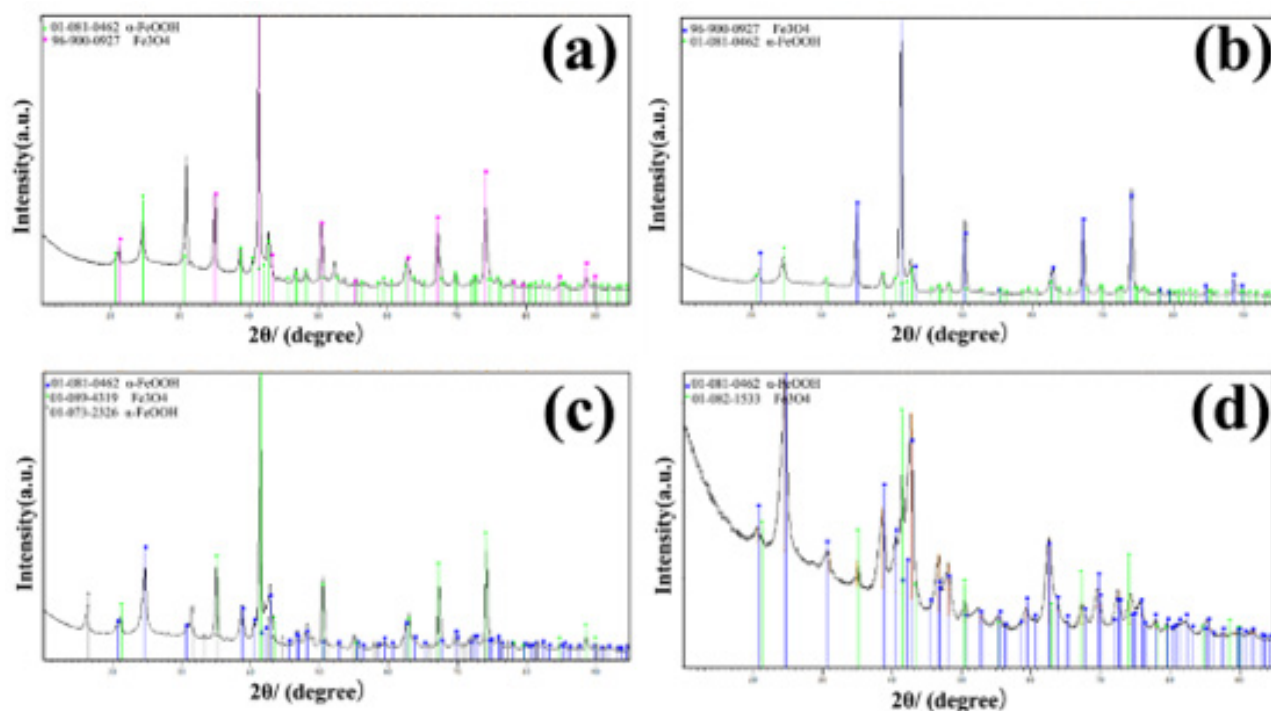


Figure 1. X-ray diffraction (XRD) patterns of (a) JK201 iron knife, (b) JK202 iron knife, (c) JK203 iron spearhead, and (d) JK204 iron knife.

logy and cultural relic protection since it can give rapid elemental data without destroying the samples.^{5,19} Twelve items were selected for the study of corrosion in the Jiangkou assemblage. The selection was based on the principle of minimizing disturbance to prevent damage to the relics. The sample information is shown in table 2. Portable X-ray fluorescence (p-XRF) was used to determine the elemental composition, while X-ray diffraction (XRD) was employed to identify the corrosion products. Portable X-ray fluorescence spectroscopy is frequently applied in archaeology and cultural relic protection since it can give rapid elemental data without destroying the samples.^{5,19}

X-ray diffraction is the usual technique used for recognizing the crystalline phases of archaeological and heritage materials. In order to investigate the mineral composition of the corrosion layers on the Jiangkou iron objects, we scraped off a little corrosion product from some chosen areas with a surgical scalpel. In total, 16 samples were taken. All samples were ground into about 200 mesh size in an agate

mortar prior to the XRD

The detailed analytical data are shown in table 3.

The experimental results (fig. 1, table 3) indicate that goethite (α -FeO (OH)) and magnetite (Fe_3O_4) are the main components in the corroded substances, while quartz is also found in some cases. The investigation on preservation reveals that some objects have corrosion layers with an inhomogeneous composition and stratification. For example, Sample JK0207 belongs to the inner layer whereas Sample JK0214 is from the outer layer. The inner sample is mainly composed of Fe_3O_4 , while the outer sample contains both α -FeO (OH) and Fe_3O_4 . Our research shows that the outer corroded layer is mainly made up of goethite with a small quantity of silica (SiO_2) and appears yellowish-brown, while the inner dark-brown layer is mainly constituted by magnetite.^{9,10} Goethite (α -FeO (OH)) has an orthorhombic crystal system, but magnetite (Fe_3O_4) crystallizes in an inverse-spinel system. Both minerals can produce dense, compact and stable layers and are usually

Table 3 XRD Results of selected iron artifacts excavated from the Jiangkou late Ming Battleground Site.

No.	Artifact Type	Artifacts No.	Lab. No.	Corrosion color	Phase	Mineral
1	Iron knife	2017PJIT2019: 6	JK0201	dark brown to black	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
2	Iron knife	2017PJIT2019: 9	JK0202	grayish-brown	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
3	Iron spearhead	2017PJIT2120: 8	JK0203	dark brown to black	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
4	Iron knife	2017PJIT1918: 4	JK0204	dark brown to black	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
5	Iron knife	2017PJIT2019: 19	JK0205	dark brown to black	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
6	Iron arrowhead	2017PJIT2725: 80	JK0206	grayish-brown	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
7	Iron object	2017PJIT2725: 85	JK0207	dark brown to black	Fe ₃ O ₄	Magnetite
8	Iron object	2017PJIT2725: 86	JK0208	dark brown to black	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
9	Iron spearhead	2017PJIT1919: 29	JK0209	dark brown to black	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
10	Iron object	2017PJIT2725: 90	JK0210	yellowish-brown	α -FeO(OH)、Fe ₃ C、Fe ₃ O ₄	Goethite, Magnetite, Cementite
11	Iron knife	2017PJIT2724: 45	JK0211	dark brown to black	α -FeO(OH)、Fe ₃ C、Fe ₃ O ₄	Goethite, Magnetite, Cementite
12	Iron object	2017PJIT2019: 24	JK0212	dark brown to black	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
13	Iron knife	2017PJIT2118: 173	JK0213	dark brown to black	Fe ₃ O ₄	Magnetite
14	Iron knife	2017PJIT2725: 80	JK0214	yellowish-brown	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
15	Iron dagger	2017PJIT2019: 34	JK0215	dark brown to black	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite
16	Iron fork	2017PJIT2118: 188	JK0216	dark brown to black	α -FeO(OH)、Fe ₃ O ₄	Goethite, Magnetite

regarded as protective phases in the corrosion of archaeological iron materials. Because iron-carbon alloys corrode electrochemically when oxygen and moisture are available, the physical character of these layers affects the rate at which deterioration continues. Dark brown to black magnetite can develop as a relatively coherent surface layer that restricts the movement of oxygen and water toward the surviving metal, thereby slowing further post-excavation corrosion to some degree.^{11,12}

The XRF and XRD analysis, and supporting analytical observations were used to assess elemental composition, object condition, and the form and distribution of the corrosion products. Taken together, the results support the following interpretations.

The assemblage is affected primarily by material loss, fractures, pits, compact concretions, mineralization, and pitting corrosion. Damage is generally most advanced at the surface, and the metallic core has been entirely consumed in some objects. Because the present storage conditions do not maintain proper humidity or oxygen environment, secondary

corrosion has also become widespread after the excavation. Corrosion products remain strongly incorporated with sand and gravel, while persistent features such as mineralization and severe surface crusts continue to happen on many objects.

Iron is the predominant metallic element in every XRF measurement, with less amounts of phosphorus, aluminum, sulfur, arsenic, titanium, and other trace elements. When the origin of an archaeological iron object is uncertain, one initial question is that whether the iron is meteoritic or derived from smelting. The presence of nickel and cobalt are commonly treated as the characteristic indicators of meteoritic iron. Neither Ni or Co was detected in the analyzed Jiangkou iron objects, the results therefore support the conclusion that the artifacts were made from smelted iron rather than meteoritic iron.

The Jiangkou iron objects spent a long period submerged in riverbed sediments, yet neither elemental chlorine nor chlorine-bearing crystalline phases were identified by the p-XRF or XRD analysis. On this basis, the assemblage

was provisionally judged not to require a desalination stage before further treatment.^{13,14}

3. Conservation and Restoration Methods

The analytical evidence, considered together with the present condition of the objects, was used to formulate the following conservation and restoration sequence for the Jiangkou iron objects assemblage.

3.1 Documentation

Documentation was prior to all physical treatments. For each object, the record included: (1) general photos and basic identifying information; (2) fine pictures of fractures, damages, cavities, pitting corrosion, concretions and other condition characteristics; and (3) microscopic examination and registration of corrosion appearance and remaining surface details by using an ultra-depth-of-field digital microscope.

3.2 Removal of Surface Attachments

Cleaning begins with the removal of loose calcium substances and proceeds to remove the corroded concretions in order to reveal the original conditions of all objects. Before removing any residues, the surface must be examined for the leftover archaeological evidences like wooden scabbards, lacquer, copper sword guards and other decorations or combined parts. The treatment methods will be chosen depending on their conditions. If there are no organic remains or decorative parts remaining, the loose deposits, dust, calcium accumulations and other impurities will be cleaned by means of a scalpel, copper-wire brush and a soft brush. Then the entire objects will be washed with deionized water and absolute alcohol. If wooden scabbars or lacquer layers exist, we shall try to retain them in their original positions. The deteriorated materials which cannot be kept on the objects will be collected, sealed in labelled containers and preserved for further study. When the conditions permit, the remaining woods and lacquers will be attached. Polyethylene glycol

400 (PEG 400) is used for preliminary fixing, and Rhoplex MC-76 might be employed if necessary to enhance the bond between the organic remains and the underlying iron.¹⁵⁻¹⁷

For the very delicate objects, the cleaning with deionized water or absolute alcohol will be avoided to safeguard the fragile archaeological evidences.

3.3 Rust Removal

The active chemical reactivity of iron resulted in excavated objects usually bearing different levels of corrosion products. Loose or actively developing rust can promote continued deterioration and must be reduced as part of the stabilization.

Loose corrosion was removed mainly by mechanical tools and methods including engraving tools, scalpels, ultrasonic dental scalers, and brushes according to different surface conditions. Where the corrosion crust was compact and strongly bonded, mechanical work was supplemented with chemical softening. A 5% aqueous oxalic-acid solution was applied on degreased cotton for one hour at a time, and the procedure was repeated at least three times. After each application, softened corrosion and chemical residues were brushed away with deionized water.^{18,19}

3.4 Drying

Because retained moisture significantly increases the corrosion rate of archaeological iron objects, every treatment involving water was followed immediately by active drying. Forced air was used to remove residual moisture from the objects as quickly as possible.

3.5 Corrosion Inhibition

A corrosion-inhibiting treatment was included to improve long-term stability. Its purpose was to create a dense protective complex on the surface and thereby reduce the effect of subsequent environmental fluctuations.

The first stage consisted of four times of brushed applications of a 3% tannic-acid solution combined with 80–85% phosphoric acid. Once the surface had dried completely, loosened corrosion was removed with a steel brush and the sequence was repeated. A phosphoric-acid-free tannic solution was then

applied four times with a stiff-bristle brush.^{20,21}

3.6 Consolidation

Structurally weakened areas were consolidated during the treatments. Rhoplex MC-76, a copolymer of butyl acrylate and methyl methacrylate, was selected for this purpose. The material has a minimum film-forming temperature of 10–12 °C, adheres effectively to concrete, masonry, brick, wood, and metal, and offers useful chemical resistance. These properties make it suitable for stabilizing severely deteriorated archaeological iron objects.

3.7 Repair of damage

Damages were repaired where intervention was needed to restore structural support and improve the visual continuity of an object.

Moulds were taken from corresponding well-preserved portions of the objects. Before moulding, original surfaces were isolated with cotton fabric or plastic film to prevent contact and contamination. Modelling clay was shaped against the protected area and allowed to cure fully. Depending on the requirements of the individual object, the fill material was a rapid-setting metal-filled repair compound, polyester body filler, or epoxy resin.^{22,23} After curing, the replacement was trimmed, shaped, and finished to follow the original form.

3.8 Retouching

After damages had been filled and the surfaces finished, repaired areas were toned to relate visually to the surrounding original corrosion. Plant-based adhesives were mixed with chloride-free natural or artificial pigments and, if necessary, acrylic paint. The purpose was to blend the repair at a normal viewing distance and make it recognizable under a close examination, in agreement with the conservation principles of reversibility and recognizability.

3.9 Protective Coating

When ideal storage conditions cannot be maintained, a surface coating can protect the object from the effects of environmental changes and atmospheric pollutants. Acrylic resins, silicones and fluorocarbons are frequently used for this purpose. Among them,

Paraloid B-72 is mostly adopted in conservation. On each object, a 1–2% solution of Paraloid B-72 in acetone is brushed, and the number of applications is changed according to the surface condition. If a greater coverage is required, more coats are applied. The final coating is expected to keep the object's surface protected without altering its colour obviously or giving an inappropriate gloss, so that the original appearance of the object can still be seen clearly.^{24–26}

4. Interpretation and heritage inheritance of the Jiangkou late Ming Battleground Site

The Jiangkou iron objects have historical, cultural, technological and aesthetic value. After systematic preservation and explanation, the objects can be viewed from various angles and exhibit many historical evidences. Scientific treatment can keep their original existence, strengthen the weak parts and preserve as much of the original authenticity as possible, providing a solid foundation for future archaeological and interdisciplinary research. Their shapes, manufacturing marks, decorations and proportional arrangements also reflect a high level of weapon-making development during the late Ming dynasty and the skills of the artisans.^{27,28} From the point of view of conservation, the long burial in water has caused extensive corrosion, mineralization and deformation on the Jiangkou objects. Without any protection, these changes will continue to affect the present materials and the evidences they contain. Therefore, the treatment plan includes recording the current condition, reducing and controlling the corrosion, reinforcing the structures, repairing the damaged parts and applying a final protective layer.^{28–30} These treatments stabilize the objects, slow down the deterioration rate and maintain the forging marks and remaining decorative details as evidence for further study. A balance is made between the technological efficiency and the principles of minimum intervention, recognizability and reversibility. The repairs are obviously different from the

original materials and the selected methods give opportunities for further treatments if needed. Thus, this programme not only extends the physical life of the unearthed iron objects but also preserves their values for investigation, exhibition, public interpretation and cultural communication. Concerning art and culture, the Jiangkou iron objects combine the practical military design with special visual characteristics. Swords, spear heads, arrowheads and axes are designed to achieve a balance between usability, convenient handling and formal harmony. Long blades with thick backs, symmetrically tapered spear heads, accurately made arrow points and evenly weighted axes show the craftsmen's skills in proportion, rhythm and composition during the late Ming dynasty. Some parts of the original surface are covered by mineralization, but the remaining hammer marks, polished traces and individual decorative features still indicate the ancient way of weapon-making. Therefore, their aesthetic value is not only reflected in their appearance but also in their structure and ergonomics, demonstrating that the practical functions and visual effects are combined in the traditional Chinese iron working technique. The visual and technical importance of the whole weapon system is obvious too. The recurrence of dimensional, proportional and weight distribution relationships suggests a degree of uniformity and standardization in the excavated materials. The shapes of spear heads and arrow heads further imply the considerations of flight stability, penetration power and tactical use. These features not only reflect the organisation of military equipment but also modify the weapon designs according to the military needs of the late Ming Dynasty. They also exhibit the craftsmen's practical knowledge of mechanics and metallurgy gained from long experiences. By studying the forms and manufacturing traces of the objects, one can restore the late Ming military technology and production, and at the same time understand the historical background where the weapons were manufactured and used.

Considering the Jiangkou project, it combines the scientific conservation with the cultural and archaeological studies. The procedure stops the iron objects from deteriorating

gradually, keeps their physical strength and preserves their historical significance. Moreover, the explanation clarifies their manufacturing methods, functional structures, decorations and artistic characteristics. Through carrying out both these works, the investigation safeguards the entire set physically and enhances its importance for research, exhibition in museums, public explanation and cultural inheritance. As an important group of the late Ming weapons and products of ironworking, the Jiangkou iron objects inform both the conservation of underwater archaeological iron objects and the study of historical weaponry technology. The integrated procedure developed here may also provide a workable model for treating and interpreting comparable archaeological iron collections.

5. Conclusion

The Jiangkou iron objects were buried for a prolonged period in an underwater environment. Complex conditions in the riverbed, followed by changes after excavation and storage, produced mineralization, compact surface attachments, pitting, cracking, and laminar exfoliation, all of which place their structural stability and long-term survival at risk. Condition assessment was combined with portable X-ray fluorescence (p-XRF) and X-ray diffraction (XRD) to investigate elemental composition, corrosion phases, and the distribution of deterioration. Goethite and magnetite were identified as the dominant corrosion products, while chlorine was not detected at a significant level. Considered together with the burial context, these observations suggest that the assemblage is not undergoing the chloride-driven corrosion typically associated with many excavated iron objects and provide the analytical basis for selecting an appropriate treatment strategy.

The procedure of treatment includes the steps of surface cleaning, rust elimination by using both mechanical and chemical methods, drying under control, corrosion prevention, repair of the damages and the final coating. In fact, this method can eliminate the damaging

corrosion and the adhered substances, enhance the structural stability and increase the reliability of the objects. It can also maintain an appropriate balance between stabilization and exhibition in the museum while preserving as many historical evidences, manufacturing characteristics and material authenticity as possible. The Jiangkou iron collection consists of iron articles found from water, therefore their conditions and corrosion behaviors are related to other archaeological collections. Hence, the analytical approaches and treatment procedures presented here can be applied to preserve similar iron objects which will be unearthed in the future. This research must follow the principles of minimum interference, authenticity and reversibility and be assisted by preventive conservation and long-term environmental observations. A comprehensive system combining scientific exploration, active

treatment and continuous surveillance will provide a better basis for the protection of archaeological iron materials and keeping their research value in the future.

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ENDNOTES

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