Investigation of Deterioration for Large Outdoor Iron Statues Relics: A Case Research of Chairman MAO Iron Statue in Qinghai, China

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Abstract: In this study, the Chairman MAO iron statue in Qinghai, China was analyzed via multi-analytical methodology, including polarizing microscope, SEM-EDS, metallographic analysis, high-resolution X-ray diffractometer, ion chromatographic analysis, silver nitrate titration detection in rust samples. The iron cultural relics are affected by factors such as their chemical composition, metallographic structure and surface characteristics, casting process, and natural storage environment. Although the corrosion rate is different, the corrosion is inevitable. With the corroborative evidence derived from the above analyses, it could be determined that the long-term preservation of cast iron statues in outdoor natural environments is prone to oxidation and corrosion, which due to the poor air circulation inside the statue of Chairman Mao Zedong, the humidity is significantly higher than that of the outside. In addition, due to the large temperature difference between day and night in this area, the condensed water is easy to form, causing the inner cavity of the statue and the welding parts to be rusted particularly seriously by the electrochemical corrosion and chemical corrosion. Compared with single chemical corrosion, electrochemical reaction can greatly accelerate the corrosion of iron. This result provided important scientific basis onto the production crafts of the precious casting, and the correlation between environment and deterioration for large outdoor iron relics, contributing to the conservators to make informed decisions on restoration.

Keywords: outdoor environment; iron statues; multi-analytical; deterioration

1. Introduction

The cast iron statue of Chairman Mao Zedong is located in Shanchuan Machine Tool Foundry, Chengbei District (North 101.767372, East 36.638486), Xining City, Qinghai Province. It was cast in 1968, the height of the entire statue of Chairman Mao is 12.26 m, the height of the main body of the statue is 7.1 m, the base surface is 960 square meters, and the total weight is 28 tons. The cast iron statue is made by welding five parts of cast iron, and the appearance of the whole body appears gray. It is one of the few cast iron statues of Chairman Mao Zedong in China. It carries the Chinese nation and the brave and tenacious national spirit, as well as the memory and commemoration of the great leader, and shows the exquisite casting craftsmanship. The statue has extremely high historical value and casting technical value. It is listed as the first batch of red revolutionary cultural relics from Qinghai Province in 2021.

Through the on-site cultural relics investigation, it was discovered that the statue is located in the courtyard of Shanchuan Community, Chaoyang West Road, Chengbei District, Xining City, Qinghai Province, and the statue is preserved in the outdoor natural environment (Location map of Chairman MAO Statue as shown in Figure 1). The entire
The statue is basically intact, but there are cracks, rust, and other diseases in many welded parts of the chest of the statue, and the surface paint has been rusted, cracked, and nailed to different degrees in the later stage. The patent leather on the inner side of the statue is cracked and the patent leather are severely damaged, it is accompanied by salt and scab. Due to its age and no intervention with any protective facilities or measures, the external surface and internal cavity of the statue have been rusted to varying degrees, the paint peeling off, and the welds had begun to show serious cracking and other diseases, which are showing a trend of gradual aggravation, therefore, the protection and restoration of the statue cannot be delayed.

Figure 1. Location map of Chairman MAO Statue in Qinghai, China.

This paper aims to use the multi-analysis method [1–13] to scientifically analyze, detect, and characterize the statue body and the occurrence environment, etc., as the basis for the analysis of the disease cause of the statue by rusting and to design the later restoration and protection plan.

2. Investigation and Experiment Methods
2.1. Research Methods
2.1.1. Investigation and Survey of Occurrence Environment

Iron cultural relics exposed to atmospheric conditions are subjected to corrosion [14], known as the atmospheric corrosion. Atmospheric corrosion is the most common type of metal corrosion. Ironware cultural relics are exposed to the natural environment for a long time, leading to corrosion which is closely related to various factors such as humidity in the environment. Therefore, by investigating the occurrence environment, including regional rainfall, humidity, dust, salt, and other pollutants, it is possible to obtain various influencing factors in the outdoor environment that may cause or accelerate the oxidation of iron cultural relics, or accelerate the aging, which can provide the research background for the cause analysis of the statue corrosion.
2.1.2. Sampling and Laboratory Analysis

By sampling the base of the statue, analyzing and testing the composition and rust products scientifically, the cause of iron corrosion of the statue and the degree of rust can be obtained to provide a scientific basis for later protection and restoration. The statue of Chairman Mao Zedong was completed by split casting, which was first cast into five parts and then spliced together. Therefore, when the samples are selected, the rust-off parts of the casting part and the middle splicing welding parts are collected separately (Figure 2).

![Sampling location of Chairman MAO Statue](image)

**Figure 2.** Sampling location of Chairman MAO Statue (The red circle is the sampling location).

2.2. Experiment Methods

2.2.1. Morphology Observed

Polarizing microscope (BX35M, Olympus Co., LTD, Tokyo, Japan) was used to observe the macroscopic morphology of different samples with magnification of 5–50 times.

2.2.2. SEM-EDS

Scanning Electron Microscope–Energy Dispersive Spectrometer (SEM-EDS) (SU3500, Hitachi High-Tech Co., LTD, Tokyo, Japan) was used to observe the microscopic morphology of the sample and detect the element composition and distribution. The sample was fixed on the platform with conductive adhesive, and the gold spraying time was set at 100 s to conduct the sample and eliminate the charge accumulation. The test conditions are vacuum mode, acceleration voltage is 15 kV, amplification is 100–300 times.
2.2.3. Metallographic Analysis

The organization evaluation, process analysis, defect research, and judgment of the raw materials of the metal materials for processing structural parts and finished products were carried out.

2.2.4. Ion Chromatographic Analysis

ICS-90 ion chromatograph (Shanghai Leirui Scientific Instrument Co., LTD, Shanghai, China) was used as the testing instrument. Grind the rust sample through an 80-mesh sieve, and dissolve 2 g in 100 mL distilled water. Shake and soak it for 7 days, and then detect the relevant ion content in the leaching solution. The measurement data analysis method adopts the general rule of JY/T020-1996 ion chromatography analysis method.

2.2.5. High-Resolution X-ray Diffractometer

The X’ PertPro MPDX-ray diffractometer (Smart Lab (9), Rigaku Co., Tokyo, Japan) was used as the analytical instrument, and the anode target was a copper target as the analysis condition (test voltage: 40 KV, test current: 30 mA, 2θ range: 5°–90°, step width: 0.02°, scanning rate: 4°/min). The experimental data analysis method is based on the JY/T009-1996 General Principles of Rotating Target Polycrystalline X-ray Diffraction Method. The X-ray diffraction experiment is carried out by powder sample method, and the diffraction spectrum is analyzed by Jade 7.0.

2.2.6. Silver Nitrate Titration Detection

Take the rust products and grind them with agate to powder. Dissolve the sample with nitric acid, after two minutes, filter with filter paper to obtain a clear solution, then add 2, 3 drops of 1% AgNO₃ solution to the clear solution and observe whether white flocs appear. The nitric acid solution used is a dilute nitric acid solution prepared in a ratio of 2:1 to the distilled water and nitric acid solution.

3. Results and Discussion

3.1. Preservation Status and Disease Type

The cast iron statue is located in Chengbei District, Xining City, Qinghai Province, in the northwest of Xining City, with an average elevation of 2275 m. The climate is a continental plateau semi-arid climate, the annual average sunshine time is 1939.7 h, the annual average temperature is 7.6 °C, and the highest temperature is 34.69 °C, the lowest temperature is minus 18.9 °C. The PM2.5 (small particulate matter) AIR quality Index in Xining was 157, the NO₂ (nitrogen dioxide) air quality index in Xining was 16, and the SO₂ (sulfur dioxide) air quality index in Xining was 16. The annual average precipitation is 380 mm, and the evaporation is 1363.6 mm; it belongs to the plateau and alpine climate. The average summer temperature is 17–19 °C, characterized by low air pressure, low rainfall, large evaporation, long freezing period, short frost-free period, large temperature difference between day and night, and sufficient sunshine. The annual average temperature is 4.9 °C, and the dry and hot climate makes the atmosphere oxidize strongly. Under such climatic conditions, long-term preservation of cast iron statues in outdoor natural environments is prone to oxidation and corrosion [15–18].

The performance of its important diseases is shown in Table 1. Through field investigation, it is found that the main diseases of the statue are corrosion cracking of welding parts and corrosion of the inner cavity. From the point of view of the incomplete position and shape, the main influencing factors of corrosion are the corrosion of the cast iron material of chairman MAO’s statue itself and the accelerated aging in the occurrence environment. In addition, the long sunshine time will also cause the cultural relics to age and accelerate the deterioration. The environment of the inner cavity and the outer surface of the statue casting structure is quite different. Due to the poor air circulation inside the statue of Chairman Mao Zedong, the humidity is significantly higher than that of the outside. In addition, due to the large temperature difference between day and night in this area, the
condensed water is easy to form, causing the inner cavity of the statue and the welding parts to be rusted particularly seriously.

Table 1. Survey of disease status of Chairman Mao Zedong statue.

| Icon Symbol | Disease Name       | Disease Description                                      | Existence Location                                      | Disease Degree |
|-------------|--------------------|--------------------------------------------------------|--------------------------------------------------------|---------------|
| R           | Rusting            | Oxidation of iron cultural relics                       | Exfoliation of the overall patent leather of the statue | General       |
| E           | Welding trace      | Traces left by welding during the early restoration of the statue | Welds on the chest, waist, and legs                      | General       |
|             | Soil attachment    | Mud attached to the statue surface that affects the appearance of the object | Statue as a whole                                       | General       |

3.2. Material Composition of Cast Iron of Statue

As is shown in Figure 3a, the results show that under the condition of not using dilute nitric acid, there are a large number of carbon inclusions, ferrite structure, and a little pearlite structure. The shape and size of ferrite grains were revealed by scanning the microstructure 500 times after corrosion (Figure 3b). A small amount of pearlite structure was distributed at the boundary of variable ferrite grains after cleaning, and the shape, size, and distribution of inclusions were observed. Figure 3c shows the pearlite structure characteristics. The observation of the experimental sample found that the metallographic structure of the sample is mainly pearlite, with the strip-shaped carbon inclusions. It shows that the cast iron of the statue is made of white iron.

![Figure 3](image-url)

Figure 3. Corrosion morphology of ((a) not erosion, (b) erosion, (c) pearlite structure characteristics).

3.3. Corroded Microstructure of the Rust

According to the results of the optical imaging analysis of the sample, there are contaminants and loose rust products on the surface of the sample. It can be observed that the density of the rust products on the surface of the ironware is low, and oxide film that can effectively protect the body is not formed on the surface of the ironware. The rust peeling off and the presence of yellow rust spots are presumed to be surface corrosion products caused by the presence of soluble chloride salts in the sample (Figure 4a,b). In subsequent experiments, the sample surface soluble salt inventory and soluble salt types will be further analyzed. In addition, the microstructure of the corrosion products in the samples is different, and the corrosion products may be different due to the different
environment where the sampling location is located. The microstructure of the corrosion products is relatively loose, and the density of the oxide layer formed on the surface of the iron is low, and contact with the air will further the corrosion process, hence the corrosion of the iron continues to deteriorate the statue.

According to Figure 4c,d, composition analysis in cast iron samples are carbon, silicon, aluminum, phosphorus, and calcium. The chemical composition of cast iron has a great influence on its corrosion resistance. The composition and content of elements in different parts of the samples are similar, and the content of main chemical components is basically consistent with that of modern standard cast iron.

Figure 4. Micromorphology and elemental compositions of the rust samples. Polarizing microscope (a,b), EDS (c,d) and XRD (e,f).

According to Figure 4c,d, composition analysis in cast iron samples are carbon, silicon, aluminum, phosphorus, and calcium. The chemical composition of cast iron has a great influence on its corrosion resistance. The composition and content of elements in different parts of the samples are similar, and the content of main chemical components is basically consistent with that of modern standard cast iron.
As shown in Figure 4, the X-ray diffractometer (XRD) pattern of 4e, the actual peak positions on the diffraction pattern are 21.266°, 26.357°, 42.660°, 44.169° respectively corresponding to the peak positions of β-FeOOH and γ-FeOOH in the standard XRD diffraction database PDF 21.223°, 26.323°, 42.956°, 43.769° indicating that the sample contains akaganeite (β-FeOOH) and lepidocrocite (γ-FeOOH); in addition, the actual peak positions on the diffraction pattern are 34.886°, 36.744°, 37.258°, 39.865°, 43.056°, 50.630°, 52.208°, 54.195°, respectively corresponding to the peak positions in the standard PDF library 35.631°, 37.250°, 38.848°, 40.378°, 43.285°, 50.008°, 53.734°, 54.926°, indicating that the sample contains maghemite (γ-Fe₂O₃) and hematite (α-Fe₂O₃). It is speculated that the sample may contain akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), and hematite (α-Fe₂O₃).

3.4. Chloride Ions in Sample

In order to determine whether there are soluble chlorides in the sample, the surface corrosion products caused by the sample surface soluble salt inventory and soluble salt species are analyzed by ion chromatography and silver nitrate titration detection.

The results shown in Figure 5 show that the collected two samples contain chloride ions, and the rust product extract of sample No. 2 contains higher chloride content; after titrating the two samples with silver nitrate solution, white flocculent precipitates appear, indicating that the samples have different concentrations of chlorides and soluble chloride salts; the white precipitate in sample No. 2 contains more white precipitates, which confirms the conclusion that it has a higher chloride content in the ion chromatography analysis.

| No. | Cl⁻  | NO₃⁻  | SO₄²⁻  |
|-----|------|-------|--------|
| 1   | 0.009% | 0.017% | 0.09%  |
| 2   | 0.018% | 0.013% | 0.18%  |

No. 1 the casting part
No. 2 splicing welding parts

Figure 5. The ion chromatography and titrating with silver nitrate solution results.

Through the above qualitative analysis, it can be concluded that although a small amount of soluble salt was detected in the corroded part of the casting part and the middle splicing welding parts sampled from the statue, due to its low content, it is only necessary
to seal the splicing welding position in the later repair and protection process, without additional desalting treatment.

4. The Degradation Mechanism

In summary, the metallographic analysis shows that the main material of Chairman Mao Zedong’s statue is gray cast iron. It can produce relatively slow graphite corrosion, which is the internal factor of the rust of the statue. According to the investigation of the occurrence environment of the statue in the early stage, the following results are obtained: It is found that the occurrence environment of the statue is harsh; the sunshine time is long; the corrosion of condensed water is caused by the temperature difference between day and night [19]; and the atmospheric corrosion may be the important factors that cause the rust of the statue. The ion chromatography test of the sample shows that the chloride ion content is between 0.009% and 0.018%; the content of sulfate ion and nitrate ion is also quite high. The silver nitrate titration analysis also found that there is chloride element in the corrosion product of the statue. Therefore, chlorine (soluble salt) is also one of the important reasons for the rust of Chairman Mao’s statue. From the X-ray diffraction pattern, the main phase of the corrosion product is akaganeite (β-FeOOH), there is a small amount of γ-FeOOH, and the γ-FeOOH is not converted to α-FeOOH. It can be inferred that the corrosion of the statue continues to occur. In addition, the XRD results also show that FeSO₄ is still present in the corrosion products, which is not transformed into a relatively stable α-Fe₂O₃; therefore, it also shows that the corrosion of the statue is still in the process of development, and the degree of deterioration will still increase. It can be seen that the statue has been exposed to the outdoor natural environment without any protection measures for a long time, so that it has accelerated the corrosion and oxidation of iron under the combined effects of environmental temperature and humidity, atmospheric pollution and soluble salts. More importantly, this corrosion continues to occur.

The formation process of iron rust disease is actually the electrochemical corrosion process of iron [20]. The degradation mechanism of the Chairman MAO Statues in outdoor environment, shown in Figure 6, is due to the poor air circulation inside the statue, the humidity is significantly higher than that of the outside. In addition, due to the large temperature difference between day and night in this area, the condensed water is easy to form, causing the inner cavity of the statue and the welding parts to be rusted particularly seriously [19]. In humid air environment, the surface of the ironware is covered by a very thin water film due to adsorption, and the weak ionization of water produces a small amount of H⁺ and OH⁻, forming a thin and weakly acidic electrolyte film on the surface of the iron, with iron as the anode and Fe₂C as the cathode, and the surface electrolyte water film acts as the external circuit, forming electrochemical corrosion. Iron acts as an anode, losing electrons; O₂ in the water film participates in the cathode reaction. The reactions are as follows: ① Fe + 2H⁺ = Fe²⁺ + H₂; ② Fe + 1/2O₂ + H₂O = Fe²⁺ + 2OH⁻; ③ Fe²⁺ + 2OH⁻ = Fe(OH)₂; ④ 4Fe(OH)₂ + O₂ + 2H₂O = 4Fe(OH)₃, carbon dioxide in the air reacts with iron hydroxide to produce reddish-brown rust.

In addition, the iron reacts with oxygen in the air to produce iron oxide, and these iron compounds are the main components of iron rust [21]. In the process of rust disease formation, hydrogen evolution corrosion and oxygen absorption corrosion exist at the same time, especially oxygen absorption corrosion has a greater impact on the galvanic corrosion of statue.

The iron statue rust disease gradually progresses from the surface to the inside. Iron statue rust disease can be prevented by (a) surface oxidation, (b) surface powder rust, (c) small amount of pitting, (d) large area pitting, (e) local rust layering. The change and development process has typical characteristics from surface to inside, from point to surface. From the analysis of the corrosion performance level, the rust layer of the iron gusset plate is divided into three layers: The first layer is the surface layer of floating rust Fe₂O₃; the second layer is the grain rust FeO·nH₂O; the third layer is the bottom rust Fe (OH)₃ and FeOOH. The rust on the upper layer is relatively loose and is a mature inert substance; the
The degradation mechanism of the Chairman MAO Statues in outdoor environment. Corrosion mechanism (a) and Condensate water circulation in the cavity of the Statue (b).

5. Conclusions

This paper performed a multi-analytical research on investigation of deterioration for large outdoor iron statues relics, to detect and characterize the statue body and the occurrence environment, etc., as the basis for the analysis of the disease cause of the statue rust and the design of the later restoration and protection. The iron cultural relics are affected by factors such as their chemical composition, metallographic structure and surface characteristics, casting process, and natural storage environment. Although the corrosion rate is different, the corrosion is inevitable. Generally, when the atmospheric environment is dry and polluted, the corrosion rate of cast iron is very slow. As time goes by, a protective film will naturally form on the surface of the casting, which makes the alloy change from an active state to an inert state, which significantly reduces the corrosion rate of cast iron in the atmosphere; on the contrary, in wet and other complex environment, the corrosion of iron will develop from single chemical corrosion to electrochemical corrosion, which accelerates the corrosion of iron. The results show that the soluble salt content of rust samples is low, and further desalination treatment is not needed. Moreover, the poor air circulation inside the statue of Chairman Mao, and the condensed water cause the inner cavity of the statue and the welding parts to be rusted particularly seriously. This is mainly due to the chemical corrosion accelerated by the electrochemical corrosion caused by the adhesion of condensed water. Therefore, in the later repair and protection management work, the focus is on the removal of rust and condensed water alleviating and management measures. Thus, the research on the correlation between environment and deterioration for large outdoor iron relics is very important scientifically formulating the protection technology route.

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