

Study on Corrosion Factors of Iron Artifacts Recovered from the Middle West Sea

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ABSTRACT

This study investigates corrosion process through analysis of corrosion products and desalination solution as a precedent study to present proper conservation treatment methods for iron artifacts collected from the middle West Sea. Depending on the environment where the iron artifacts were buried underwater, the corrosion patterns may be different. In order to treat the heritage stably and effectively for conservation, the major corrosion factors and information to remove or control the factors should be obtained. The underwater environment is rich in water, oxygen and salt, and it is very easy for iron artifacts to be corroded. In an environment where oxygen supply is little like seabed mud, anaerobic corrosion may occur. The iron artifacts in the seabed may be deeply buried in the mud or exposed on the surface of the seabed. This study intends to obtain information on the corrosion pattern of iron artifacts collected from the seabed surface of middle West Sea. In addition to those deeply buried in dense silt, there are also cases of recovering those exposed on the seabed or shallowly buried in the surface layer. In this study, we obtained information on the corrosion patterns of iron artifacts recovered from the seabed layer in the central West Sea. The samples used in the study were corrosion products from iron artifacts excavated from waters of Mado, Taean and of Seomeopbeol, Ongjin and desalination solution and the major components of corrosion products and anions of desalination solution were analyzed using Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) and X-ray Diffraction (XRD), Ion Chromatography (IC). The analysis result shows that major components including P, S and Mackinawite (FeS) were identified as compounds related to it. In the desalination solution, high concentration of Cl^- and SO_4^{2-} was measured. It is expected that this study result can be utilized as essential data for establishing methods for effective and systematic conservation of iron artifacts excavated from underwater and it is intended to continue additional studies such as analysis on corrosion product of iron artifacts recovered from various waters and corrosion reproduction experiment through collaboration with various fields.

Keywords: middle West Sea, iron artifacts, corrosion factor, corrosion product

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INTRODUCTION

Middle West Sea is a place where underwater cultural heritage is buried. Along the Taean coast Goryeo celadon was net-caught while fishing octopus by Ongjingun Seomeopbeol, Ansansi Daebudo and Hwaseongsi Jebudo in Korea. In particular, five shipwrecks from Goryeo and Joseon dynasties were discovered and surveyed in the Taean offshore of Chungcheongnam-do for eight years from 2007 to 2015 and historic ships from early and mid-eighth century was discovered in the waters of Seomeopbeol in Incheon in 2013. Iron pots, which were used as kitchenware by crew or carried as cargo, were lifted.

Underwater environment is rich in water, oxygen and salt where iron artifacts are easily corroded. In addition, in an environment where oxygen supply is low like in the mud, anaerobic corrosion may occur by sulfate reducing bacteria. Therefore, the corrosion patterns of iron artifacts may be different in the underwater environment depending on each condition or various factors. In order to conserve damaged iron artifacts effectively and stably, information on how to remove or control major factors that influence corrosion should be obtained.

CORROSION OF IRON ARTIFACTS IN UNDERWATER ENVIRONMENT

Cl⁻ and SO₄²⁻ are dissolved in seawater at about 19 gr and 2.6 gr per 1 L (1 gr = 0.0684 g), and their high electrical conductivity promotes corrosion of iron artifacts (Baek Young-Nam and Yeo Woon-Hwan 1980, 673). Deposits formed on the surface of iron artifacts are removed by the high flow rate of the environment, and corrosion can be accelerated (Japanese Standards Association 1984, 33). Due to these various factors, iron artifacts are actively corroded in the seabed environment, concretion, a very hard foreign substance is formed on the surface. According to previous studies, the main component of concretion is CaCO₃, and iron artifacts are corroded and it is the clump of organisms and shells and surrounding mud. Concretion is densely formed and corrods independently from the external environment and the process is as follows (North and MacLeod 1987, 76-78):

1. Reduction reaction occurs with the formation of cathode in an isolated water in the concretion.
2. An anode is formed on the surface of iron artifacts, releasing Fe²⁺ and Fe³⁺ with oxidation reaction, resulting in creation of acidic solution at pH 4-5.
3. Hydrolysis of Fe²⁺ + H₂O → Fe (OH)⁺ + H⁺ by acidic solution.
4. FeCO₃ is formed as part of Ca²⁺ in CaCO₃ of concretion is interchanged with Fe²⁺.
5. Part of CaCO₃ is dissolved by Ca (HCO₃)₂ that includes H⁺, increasing pH concentration of the surrounding environment.
6. As the pH concentration rises, oxides, hydroxides and hydroxide chlorides such as Fe²⁺ and Fe³⁺ are gradually eluted.
7. During steps one to six, CaCO₃ condensate is gradually dissolved and hard iron cementing is formed.

In addition, anaerobic corrosion can occur in places where oxygen is scarce, such as deep in the mud of the seabed environment. The typical example of anaerobic corrosion of iron artifacts is corrosion by sulfide reduced by sulfate reducing bacteria ($4\text{Fe} + \text{SO}_4^{2-} + \text{H}^+ \rightarrow 3\text{Fe}^{2+} + \text{FeS} + \text{H}_2\text{O}$). The resulting corrosion forms black iron sulfide, which is oxidized in red when exposed to the atmosphere (Fujii 2009, 50-51).

METHODOLOGY

In this study, desalination solution (Sodium Sesquicarbonate 0.1M aqueous solution) used during the conservation treatment of iron pots collected from Mado, Taean, Chungcheongnamdo and waters of Seomeopbeol, Ongjin, Incheon and corrosion products removed from the surface, were used as samples. The iron pots from the Mado were discovered through visual exploration of the sea bottom and part of the surface layer of the sea bottom by divers during wide-area exploration in 2011 (NRIMCH 2017, 27). Iron pots collected from Seomeopbeol were recovered from the sand and shell layer identified during the southeast Shingoji probe survey in the first underwater excavation survey in 2012 (NRIMCH 2014, 33-34).

The components of corrosion product samples were analyzed using Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) and the external characteristics of the point where certain components (P, S) were detected were observed. Then they were powdered and the compound was identified through X-ray Diffraction (XRD) analysis. Concentration of desalination solution was measured using Ion Chromatography (IC) to measure concentration of anions (F⁻, Cl⁻, SO₄²⁻, NO₃⁻, PO₄³⁻) to identify the relationship between SEM-EDS and XRD analysis result.

The number of corrosion product analysis samples was 16 in total (eight from Mado and the others from Seomeopbeol) and the points (55 points in Mado and 41 points in Seomeopbeol, 96 points in total) subjected to SEM-EDS analysis were selected with 40x magnification of stereoscopic microscope images were recorded using digital recording device attached. Conditions of SEM-EDS analysis include voltage of 15-20 kV, WD 10 mm, spot size 25, measurement time of 60 seconds and magnification up to 9,000 times. Conditions of XRD analysis for 16 powdered samples after

SEM-EDS and one additional sample (corrosion product of iron pot from Mado shipwreck no. 4) were voltage of 40 kV, current of 30 mA, and target Cu.

For desalination solution analysis, 16 samples (eight from Mado, the others from Seomeopbeol) were prepared and anion concentration was measured using IC. As Cl⁻ concentration of the desalination solution sample was expected to be very high, it was diluted with ultrapure water 100 times and cellulose filter was used to remove impurities in the sample and then anion analysis was conducted.

STUDY RESULTS

Analysis of corrosion product

When sulfate reducing bacteria is involved in the corrosion process, the high content of phosphorus and sulfur may be detected in the corrosion products (Lee Yong-deuk et al. 1996, 256), SEM-EDS analysis was conducted to check whether these two components are detected and their content. The results of analyzing corrosion products showed that sulfur was detected in 15 samples except for one sample from Mado (MD6). The maximum sulfur level was 63.61 wt per cent (MD8) in samples from Mado and 25.13 wt per cent (SE7) in samples from Seomeopbeol sea area and other samples contained 0.64~23.02 wt per cent. Among them MD8 is characterized by maximum sulfur content of 11.51 wt per cent and phosphorus content of 12.17 wt per cent. This result can be interpreted that sulfate reducing bacteria influenced the corrosion process of iron pots collected from Mado and Seomeopbeol. However, these compounds were identified with the identification of mackinawite (FeS) in MD1 and other samples identified iron oxides such as siderite (FeCO₃) or goethite (FeOOH) formed by the influence of concretion.

Table 1. Results of analysis on corrosion product of iron pot recovered from Mado (EDS, XRD)

Sample	Maximum content of major ingredient (wt per cent)			Compound Name (Chemical Formula)
	P	S	Ca	
MD1	-	11.85	10.12	Magnetite (Fe ₃ O ₄) calcite (CaCO ₃) mackinawite (FeS)
MD.2	-	1.40	0.51	Magnetite (Fe ₃ O ₄) siderite (FeCO ₃)
MD3	-	2.53	-	Siderite (FeCO ₃)
MD4	-	6.65	-	Siderite (FeCO ₃)
MD5	-	1.54	-	Magnetite (Fe ₃ O ₄) quartz (SiO ₂)
MD6	-	-	-	Magnetite (Fe ₃ O ₄) siderite (FeCO ₃)
MD7	-	63.61	-	Siderite (FeCO ₃)
MD8	12.17	11.51	-	Magnetite (Fe ₃ O ₄)

Table 2. Results of analysis of corrosion product of iron pot recovered from water Seomeopbeol sea area (EDS, XRD)

Sample	Maximum content of major ingredient (wt per cent)			Compound Name (Chemical Formula)
	P	S	Ca	
SE1	-	0.64	1.36	Siderite (FeCO ₃) magnetite (Fe ₃ O ₄) goethite (FeOOH)
SE2	0.27	1.11	3.63	Siderite (FeCO ₃)
SE3	-	2.96	0.48	Siderite (FeCO ₃) magnetite (Fe ₃ O ₄)
SE4	-	0.87	1.51	Siderite (FeCO ₃) goethite (FeOOH)
SE5	-	8.48	4.09	Magnetite (Fe ₃ O ₄) goethite (FeOOH)
SE6	0.17	4.04	-	Goethite (FeOOH)
SE7	-	25.13	37.80	Siderite (FeCO ₃) magnetite (Fe ₃ O ₄)
SE8	-	23.02	31.61	Siderite (FeCO ₃) magnetite (Fe ₃ O ₄) goethite (FeOOH)

Iron sulfide such as Mackinawite or pyrite (FeS_2) are formed together with oxides such as FeOOH , serving as the evidence to show corrosion by sulfate reducing bacteria (Lee Jae-ik and Seo Myeong-po 1992, 63), but this study did not obtain results with unique characteristics. However, according to previous studies, iron sulfide in a honeycomb structure, which is easily oxidized to calcium sulfate in the form of iron crystals, was observed in European old ships using iron nails (Kim Yong-han 1987, 151-152), SEM observation confirmed similar type of corrosion products in SE5 and SE7. In addition, samples from Seomeopbeol contain large amounts of Calcium and SE7 and SE8 showed high concentration of sulfur so it is considered to be the result of oxidation of iron sulfide. However, in the XRD analysis, the identification of relevant compounds (CaSO_4 , etc.) was not done and SEM observation did not confirm unique characteristics, requiring further research on this matter.

Analysis of desalination solution

Sixteen samples were collected from desalination solution from six pots, three from each area including MT64 and SE405 where corrosion product analysis sample was collected (red square in Table 3 and 4) to conduct anion analysis. The analysis results showed that Table 3 and 4 Cl^- and SO_4^{2-} concentration was higher overwhelmingly than other anions and EDS ingredient analysis showed 20 ppm or higher PO_4^{3-} in the MT64 sample where phosphorus was detected. PO_4^{3-} was measured in the sample from primary desalination solution of YDS1 and YDS on December 4, 2013 once respectively but it was not identified in samples after that.

Table 3. Results of analyzing desalination solution of iron pot excavated from Mado (IC)

Sample (date)	Anion concentration (ppm)				
	F^-	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}
M3S262 ('12.3.15)	0.18	60.74	241.41	-	-
M3S262 ('12.5.24)	0.16	48.11	104.80	-	-
M3S262 ('12.6.28)	0.14	30.24	72.29	3.49	-
MS76 ('12.4.25)	0.20	14.54	41.83	-	-
MS76 ('12.6.7)	0.37	13.96	40.22	-	-
MS76 ('12.7.12)	0.28	14.33	29.56	-	-
MT64 ('12.3.22)	0.28	223.83	271.22	-	25.44
MT64 ('12.5.16)	0.25	109.66	194.79	-	22.64

Table 4. Results of analyzing desalination solution of iron pot excavated from Seomeopbeol (IC)

Sample (date)	Anion concentration (ppm)				
	F^-	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}
SE403 ('14.1.7)	0.12	41.05	100.64	-	-
SE403 ('14.3.5)	0.27	13.62	17.19	-	-
SE403 ('14.5.13)	0.07	10.79	7.66	6.00	-
YDS1 ('13.12.4)	0.77	1530.31	84.31	3.97	16.27
YDS1 ('14.8.5)	0.01	172.80	27.17	-	-
YDS1 ('15.4.7)	0.01	110.51	54.32	-	-
YDS4 ('13.12.4)	0.46	439.99	48.19	-	15.68
YDS4 ('14.4.17)	0.05	55.61	10.04	7.19	-

As presented in Table 3 and 4, SO_4^{2-} was clearly detected in the desalination solution from the two sites. Generally, Cl^- dissolution is the focus in the process of stabilization considering the impact of sea water containing large amounts of salt for iron artifacts excavated from underwater but as shown in the result, whether SO_4^{2-} remains or not should be checked mandatorily.

CONCLUSIONS

This study was conducted to obtain information on effective methods of conservation treatment by analyzing corrosion products of iron artifacts collected from the Middle West Sea and desalination solution. The iron artifacts recovered from waters included artifacts lifted by removing strong and dense mud layers and artifacts buried near the surface layer or exposed on the seabed surface. In order to find out the pattern of corrosion of iron artifacts, wide area exploration of waters of Mado, Taean and excavation survey in waters of Seomeopbeol, Ongjin were conducted and the corrosion product of iron pots lifted and desalination solution were used as samples for research. In the iron corrosion process, when sulfate reducing bacteria is involved, significant amounts of sulfur and phosphorus can be detected. Therefore, in this study, SEM-EDS analysis was conducted for the components of iron pot corrosion products from Mado and Seomupbeol.

Previous studies on iron test piece corrosion by seawater, mud (collected from Mado) and Na₂S water solution, ingredients such as Sulfur or Phosphorus were not detected at all (Kim Taek-joon 2013, 47-50).

In our SEM-EDS analysis on corrosion products, a large amount of sulfur was detected in most samples and one sample from Mado contained 12.17 wt per cent of phosphorus. Sulfate reducing bacteria is confirmed in the process of iron pot from Mado and Seomupbeol. However, in the XRD analysis, there were no clear results except for the identification of mackinawite (FeS) in one sample. In the anion analysis of desalination solution, highly concentrated Cl⁻ and SO₄²⁻ were measured and it is considered to be related to the identification of sulfur as the main ingredient of corrosion products. Sulfur and SO₄²⁻ were major factors that influence the corrosion of iron artifacts collected from the Middle West Sea. However, it was not possible to obtain specific information on how these factors are involved in corrosion of iron artifacts. Follow-up research will involve sulfate reducing bacteria and further analysis of corrosion products of iron artifacts collected from various sea areas.

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