CHARACTERISTICS OF EMISSION SUBSTANCES BY ACID-DEGRADATION OF SHINAN WRECK, REPUBLIC OF KOREA

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Abstract

The Shinan wreck, Korea's first excavated underwater shipwreck in 1976, has proven an ongoing problem with acid-degradation. Acid-degradation is known as the reaction that occurs when sulfur, iron compounds, polyethylene glycol (PEG), and oxygen is placed in an environment of high humidity. As a result of this reaction, some acidic substances are produced as by-products. However, what kinds and how much of the substances emitted from the acid-degraded, waterlogged wood are the question. In this study, the characteristics of substances emitted from wooden pieces from the Shinan wreck were analyzed qualitatively and quantitatively by divided into the acid-degraded group and the degradation-free group. For the analysis, the bag test method was applied for the emission test. As results, it was confirmed that the acid-degradation affects the emission of volatile organic compounds (VOCs), formaldehyde, sulfur dioxide, and nitrogen oxide. In the case of VOCs, acid-degradation plays an important role for emitting natural VOCs such as calamenene, amorphane-A, junipene, selinane, etc., which are known to be emitted from Cryptomeria japonica in particular. Also, it seems that formaldehyde is created by the oxidative degradation of PEG and wood polymers. As it is confirmed that the emission source of formaldehyde, sulfur dioxide, and nitrogen oxide is the Shinan wreck, specifically due to the acid-degradation, applying for the de-acidification treatment on the acid-degraded parts of the wreck is necessary to mitigate harmful substances with humidity control in the shipwreck gallery.

Keywords: Shinan wreck; Acid-degradation; Bag test method; VOCs; Formaldehyde; Sulfur dioxide; Nitrogen oxide

Introduction

The Shinan wreck was an early 14th-century Chinese ship used for international trade and was discovered in the waters of Shinan-gun, South Korea in 1976. With a remaining length and width of 27m by 7m, the Shinan wreck sunk in the waters of Shinan-gun, South Korea while sailing from Ningbo, China to Hakada, Japan. Since the discovery of this old ship, a wide variety of artifacts including 23,502 pieces of relics, 28 tons of antique Chinese coins, and more had been recovered over a period of 9 years.

Conservation treatments on the recovered shipwreck spanned a period of 18 years from 1981 to 1999. As a result of an analysis on the species of tree used for various parts of the ship, the "Yonggol" - a piece that runs from the bow all the way to the stern of a ship - and the boards of the ship body were found to have been made of Pinus massoniana (Masson's pine), a tree that grows natively in the southern part of China. Also, the Shinan wreck's "Popanjae", a board

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designed to prevent the main board from directly coming in contact with seawater, was identified as being Cryptomeria japonia (Japanese cedar) [1].

The preservation process for these pieces of the ship included a 2-step polyethylene glycol (PEG) treatment method. During the hardening process, a concentration of up to 20% PEG-400 of low molecular weight was used, followed by PEG-4000; the process was finished at a concentration of 70-80% [1]. After the preservation process of the ship was completed, the body was restored by putting the various pieces back together and has been on display at the National Maritime Museum since 2004 (Fig. 1).

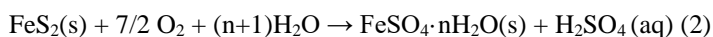**Fig. 1.** The hull of the Shinan wreck in the National Maritime Museum, Mokpo

Unlike traditional Korean ships, the Shinan wreck used iron nails instead of wooden nails to connect the respective parts of the ship body. For this reason, when the Shinan wreck was discovered, iron oxide had already permeated deep into the wood near the iron nails, and the preservation treatment was carried out without fully being able to remove the iron oxide in the wood. This iron oxide later became one of the major components of acid-degradation in the Shinan wreck (Fig. 2).

Fig. 2. Acid-degradation symptom observed in the middle part of portside (left) and upper part of starboard (right) of the Shinan wreck. By-products of the acid-degradation crystallized and then destroyed the hull of the wreck

Acid-degradation in the Shinan wreck was first confirmed in 2010, after which basic research began from 2012 to 2016 so as to determine how to de-acidify the affected parts of the ship. This research involved an investigation of the fundamental mechanisms of acid-degradation, basic experiments on treatment methods for de-acidification, monitoring surface change of the degraded parts of the ship, and a simple survey of the atmospheric environment. Through this basic research on the mechanisms of acid-degradation in the Shinan wreck, an

acidic reaction was found to occur when the iron oxide and sulfur inside the wood was submerged underwater and further exposed to an environment of high humidity; the wood was degraded, causing the production of acidic powder and acidic compounds such as sulfides to be emitted into the surrounding atmosphere [2]. It was also found that the sulfuric components in the wood were due to the sulfur, which was produced by the metabolite of anaerobic bacteria, that permeated into the wood [3]. According to a previous report of acid-degradation on the Vasa wreck, researchers found out that iron nails became the catalyst for the whole reaction. In this process, sulfuric acid and its anion are produced as a by-product of the acid-degradation. This example is shown by Eq. (1) [4] and Eq. (2) [5].

$$S(s) + 3/2\ O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \tag{1}$$

$$FeS_2(s) + 7/2\ O_2 + (n+1)H_2O \rightarrow FeSO_4 \cdot nH_2O(s) + H_2SO_4\ (aq) \tag{2}$$

During the research on the de-acidification treatment for the acid-degradation of the Shinan wreck, basic application experiments for de-acidification treatments using ammonia and sodium sebacate poultices were performed. Through the experiments, ammonia gas was confirmed to be effective in reducing the acidity of the degraded wood; note, however, that the surface of the wood turned red after the treatment, the pH dropped again over time, and the residual ammonia affected the hemicellulose in the wood [2]. As for the sodium sebacate poultice, the sample surface neutralized after the treatment and the pH level increased to almost neutral. The sodium sebacate poultice treatment was effective in removing the iron (Fe) and sulfur (S) ions, which were the main factors in the degradation [2].

Despite consistent endeavors in research, there are many problems that remain unresolved regarding the Shinan wreck and its ongoing acid-degradation. Nothing has been resolved concerning the true nature of the harmful substances emitted from the acid-degradation in addition to an optimized treatment for the acid-degradation on the degraded parts of the ship. Under these circumstances, the National Research Institute of Maritime Cultural Heritage launched a research project in 2018 aimed at accurately grasping the substances emitted from the acid-degradation of the Shinan wreck. In this study, quantitative and qualitative analyses were conducted to determine the characteristics of the harmful substances emitted from the Shinan wreck depending on the degree of degradation.

Materials and Methods

Since there is no specified test method on the evaluation of substances emitted from an old ship's pieces, the test method on emission from the VOCs of automotive parts as specified by the International Organization for Standardization (ISO) was applied [6]. For the collection and analysis of VOCs and carbonyl compounds, the ISO experiment method was also used [7-8]. For the identification of the harmful substances emitted, quantitative and qualitative analyses were conducted as to determine whether VOCs, carbonyl compounds, sulfur dioxide, and nitrogen oxide were emitted or not.

Selection of test piece

The ship body pieces for the emitted substance test were divided into Group Ⅰ, pieces which saw no degradation observed, and Group Ⅱ wherein the degradation progressed from the PEG-treated "Popanjae", a board designed to prevent the main board from directly coming in contact with the seawater, of the Shinan wreck. On the parts of the Shinan wreck where the degradation is ongoing, yellow powder is produced on the surface as a result of the degradation; the average surface pH of this powder is 2.5 or less. Consequently, in order to determine whether the degradation is underway or not for certain pieces of the ship's body, the existence of said yellow powder through visual inspection and surface pH were used as the criteria for the

selection basis (Table 1). According to the ISO test method on the VOCs of automotive interior materials, a test piece of 100cm^2 were needed. Given the size of Popanjae of the Shinan wreck, three test pieces belonging to Group Ⅰ were cut to the dimensions of 10×10×2cm, whereas the three pieces belonging to Group Ⅱ were cut to the dimensions of 8×12×2cm.

Table 1. Criteria of selection for test piece for the emitted substance test

Division	Selection criteria	Dimension
Group Ⅰ (n = 3)	· Shinan wreck pieces with no degradation · Average surface pH (as measured at 6 different points) of 4.0 or more	10×10×2cm (W×D×T)
Group Ⅱ (n = 3)	· Shinan wreck piece with degradation ongoing · Average surface pH (as measured at 6 different points) of 2.5 or less	8×12×2cm (W×D×T)

Pretreatment of test piece

For the bag test and analysis, the emissions released from the ship pieces were collected after going through the pretreatment process as described in figure 3. The pretreatment process of the test pieces preceded as follows: (A) Prepare a polyethylene bag with a capacity of 10 L. (B) Cut the end of the bag and put the test piece into the bag. (C) Seal the bag using a sealing machine. (D) Fill the bag with 5 L of nitrogen and secure the cap to seal the bag. (E) Put the bag in an oven at 65℃ and heat for 2 hours. (F) For the analysis of VOCs and carbonyl compounds, collect the air around the test piece using a Tenax tube and DNPH cartridge, respectively. Analyses of sulfur dioxide and nitrogen monoxide/carbon monoxide were conducted by directly injecting the air into GC-PFPD and Maxilizer NG, respectively.

Fig. 3. The collection of air process of test piece for the test and analysis

Instrumental analysis of VOCs

In this study, benzene, toluene, ethylbenzene, and xylenes (BTEX) were mainly analyzed; for the total volatile organic compounds (TVOC), any and all VOCs between n-hexane and n-hexadecane were included. The concentrations of other VOC substances other than BTEX were calculated with the slope of toluene. To analyze the emission concentration of VOCs from the ship body pieces, 1L of air was adsorbed using the Tenax tube (Tenax-

TA:KT50601, kNR, South Korea), and gas chromatographic-mass spectrometry (GC-MS) (Shimadzu, Tokyo, Japan) analysis followed. The conditions for the detailed analysis of GC-MS are described on Table 2. The liquid-state standard sample (Custom VOC std. 1000ppm, New Haven, USA) was used for the quantitative analysis of the calibration curve on the VOCs' concentration. The slopes of the calibration curves for BTEX were 0.989 or more.

Table 2. Analysis condition of GC-MS for VOCs analysis

Thermal Desorption		Perkin-Elmer Turbo Matrix 650
Low-temperature concentration device		Split ratio 10:1, -30℃ (Low), 30℃ (High)
Thermal desorption device		Splitless mode, Flow: 40mL/min, 290 ℃ (10min)
GC/MS		QP2020 (Shimadzu, Tokyo, Japan)
Column		DB-1 (60m length, 0.32mm ID, Film 1.00μm)
Carrier Gas and Flow		He (99.999%), 1.5mL/min
Temperature Program	Initial temperature	50℃ (8 min)
	Temperature program	6℃/min → 120℃ (10 min) → 6℃/min
	Final temperature	270℃ (5.33min)
MS Condition	Mode	EI (electron ionization)
	Electron energy	70eV
	Detection mode	TIC (Scan), m/z: 35~350

Carbonyl compounds analysis

For the analysis of carbonyl compounds, a total of 8 kinds of carbonyl compounds such as formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde, isovaleraldehyde, and valeraldehyde were analyzed in quantitative terms. For the air collection of ship piece, 3.0L of air in the polyethylene bag was adsorbed using a 2,4-dinitrophenylhydrazine (DNPH) cartridge (Sibata, Saitama, Japan). From the adsorbed DNPH cartridge, 5 mL were extracted using acetonitrile (ACN), which were then divided into 2 mL vials and analyzed using high-performance liquid chromatography (HPLC) (Shimadzu, Tokyo, Japan). The analysis conditions of HPLC are described in table 3. The slope of the standard solution's calibration curve for the qualitative analysis of carbonyl compound materials (Aldehyde/Ketone DNPH Mix-15 ppm, Supelco, Bellefonte, USA) was 1.000 for 8 kinds of carbonyl compounds, indicating very excellent calibration result.

Table 3. Analysis conditions of HPLC for carbonyl compounds analysis

HPLC	LC-20A Series (Shimadzu, Tokyo, Japan)
Detector	UV/vis 360 nm
Column	C18 Column (250 mm Length × 4.6 mm ID)
Mobile phase	Mobile bed A:B:C (Water/Acetonitrile/THF) 0 min (50/38/12) → 8 min (48/40/12) → 13 min (48/40/12) → 25 min (32/60/8) → 26 min (50/38/12) → 35 min (50/38/12) → 40 min (50/38/12)
Analysis time	40 min
Injection volume	20 μL
Column Temperature	40 ℃
Flow rate	1.0 mL/min

Sulfur dioxide analysis

A gas chromatographic-pulsed flame photometric detector (GC-PFPD) (Varian CP-3800, Perkin Elmer, USA), equipped with a CP-SIL 5CB (60m Length, 0.32mm ID, Film 3μm) column was used to evaluate the amount of sulfur dioxide emitted from the acid-degraded piece. Helium (99.999%) was used as the carrier gas with a flow of 2.0mL/min. For the temperature program of the analysis, the temperature was raised from 35℃ up to 200℃; 35℃ for 5 min → 5℃/min → 150℃ → 10℃/min → 200℃ for 7min. Before analyzing the collected

air sample, calibration was carried out with the standard substance of sulfur dioxide (10ppm, Rigas, Daejeon, Korea); the slope of the standard substance calibration curve obtained was 0.984. For the analysis of sampled air, 1 mL of the collected air was fractionated and injected into the analyzer.

Analysis of nitrogen monoxide

To evaluate the amount of nitrogen monoxide emitted, Maxilizer NG (Afriso, Güglingen, Germany) an analysis using an electrochemical measurement method was conducted. The analyzer used had a measurement range of 0-1000 ppm for nitrogen monoxide and passed the accuracy test of Korea Environment Corporation on 2nd June 2017.

Results and Discussions

VOCs

The average concentration of TVOC emitted from the acid-degraded Shinan wreck pieces were $1031.3 \pm 251.3 \mu g/m^3$ and $7495.9 \pm 1693.9 \mu g/m^3$ for Group Ⅰ and Group Ⅱ, respectively. From the 6 samples analyzed, calamenene appeared in the largest proportion among the individual VOCs. The calamenene concentrations of Group Ⅰ and Group Ⅱ were $469.8 \pm 202.4 \mu g/m^3$ and $5295.1 \pm 976.4 \mu g/m^3$, respectively. These represent 45.6% and 70.6% of the TVOC, respectively. In addition, the average concentration of amorphane-A, endo-isocampahne, junipene, and selinane were $79.0 \pm 34.5 \mu g/m^3$ (7.7%), $15.2 \pm 26.3 \mu g/m^3$ (1.5%), $39.7 \pm 29.7 \mu g/m^3$ (3.8%), $37.8 \pm 16.7 \mu g/m^3$ (3.7%) in Group Ⅰ and $443.9 \pm 129.0 \mu g/m^3$ (5.9%), $173.4 \pm 64.2 \mu g/m^3$ (2.3%), $57.9 \pm 14.3 \mu g/m^3$ (0.8%), $482.2 \pm 163.1 \mu g/m^3$ (6.4%) in Group Ⅱ, respectively. As represented on Table 4, the major VOCs in the acid-degraded Group Ⅱ showed much higher emission than those of degradation free Group Ⅰ. These results indicate that the acid-degradation of the Shinan wreck affect the emission of VOCs.

The proportion of calamenene among the VOCs was extremely high considering the fact that the composition of calamenene was 1.3% from the fresh wood of Cryptomeria japonia (Japanese cedar) in the previous research [9]. Also, the VOCs emitted from the affected ship pieces tested seem to be the result of the degradation of wood polymers. A research conducted by the university of Tokyo found that the proportions of cis-calamenene, amorphane-A, and selinane were 11.6%, 8.5%, and 4.3%, respectively from bogwood of Cryptomeria japonica, which was preserved for 3500-3800 years in volcanic ash whereas the proportion of cis-calamenene from the fresh wood was 1.9% [10]. In this study, amorpahne-A and selinane were not detected from the fresh wood of Cryptomeria japonica. They concluded that composition difference between the fresh and archaeological wood maybe due to diagenetic transformations within wood.

It should also be noted that BTEX, which exist in the largest proportion among indoor air pollutants [11-13], were not detected at all from the tested ship pieces (Figure 4). We also conducted the monitoring of VOCs in the exhibition hall with passive samplers for 10 months in 2018. The mean concentration of TVOC was $94 \pm 31 \mu g/m^3$ in the exhibition hall [14]. In this monitoring, the concentrations of BTEX were $2.6 \pm 1.0 \mu g/m^3$, $18.9 \pm 7.2 \mu g/m^3$, $5.4 \pm 2.3 \mu g/m^3$, and $3.9 \pm 1.5 \mu g/m^3$, respectively. Therefore it can be concluded that the BTEX detected in exhibition hall did not originate from the Shinan wreck. On the other hand, the aromatic compounds emitted from the Shinan wreck possibly affected the air quality in the exhibition hall.

In particular, sulfur dioxide was detected at a major emission peak from all 6 samples analyzed; it was not included in the VOCs category, however, and it was not considered when calculating the concentration (Fig. 4).
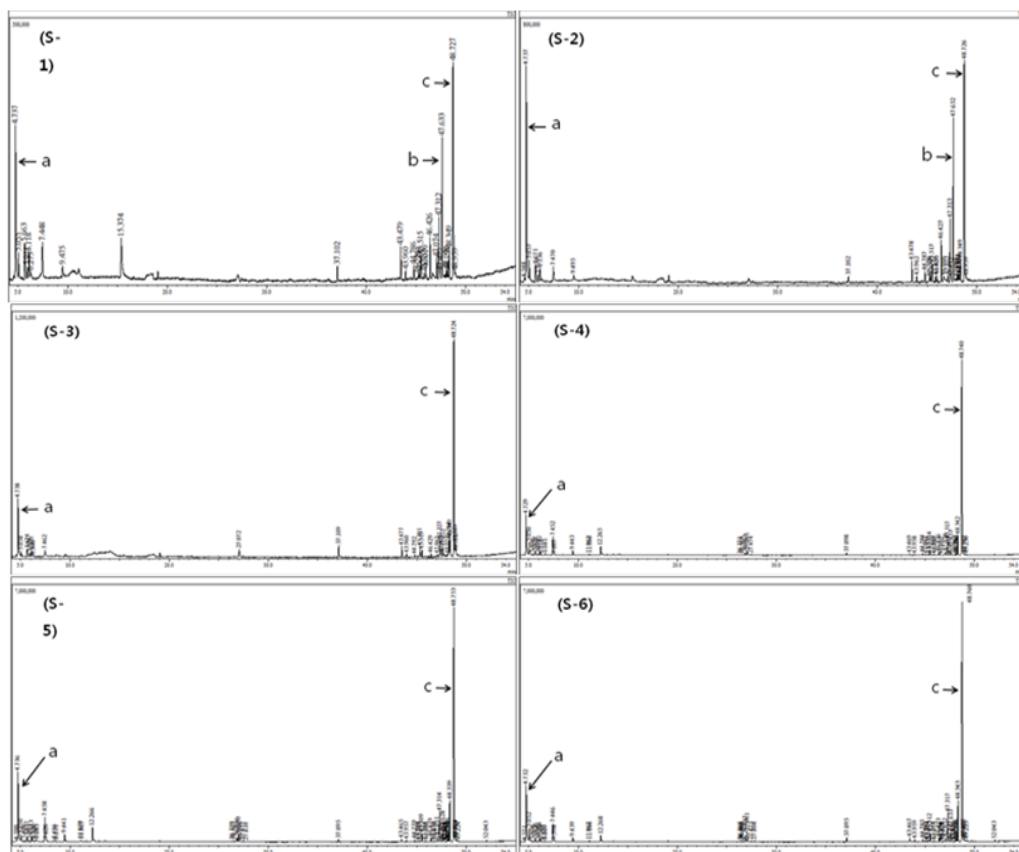
Fig. 4. Chromatograms of GC-MS analysis of VOCs inside the Shinan wreck. BTEX, the most abundant VOCs indoor, were not detected at all from the 6 samples tested. Group I: without degradation (S-1~3), Group II: with degradation (S-4~6) (a) Sulfur dioxide, (b) Junipene, (c) Calamenene

Table 4. VOCs concentrations of Group I and II. (unit: $\mu g/m^3$)

Group Compound	Group I			Group II		
	S-1	S-2	S-3	S-4	S-5	S-6
TVOC	742.7	1202.5	1148.5	5562.7	8205.3	8719.8
Amorphane-A	69.7	117.1	50.1	295.5	528.7	507.6
Calamenene	276.0	453.6	679.8	4178.8	5716.6	5990.0
Endo-Isocamphane	N.D	N.D	45.5	115.0	162.9	242.3
Junipene	41.3	68.5	9.2	41.5	64.4	67.8
Selinane	23.5	34.6	56.1	293.9	577.7	575.0

Carbonyl compounds

For carbonyl compounds, the emission concentration was confirmed to be much higher for Group II, where the degradation was ongoing compared to that of Group I, which did not show any sign of degradation (Table 5). Especially when looking at formaldehyde and acetaldehyde and their higher concentrations of emission, the concentration of Group II reached a level that was 2~4 times higher than that of the degradation-free Group I.

The average concentration of formaldehyde in Group II ($180.2 \pm 82.7 \mu g/m^3$) was below the environmental standards ($210 \mu g/m^3$) established by the Ministry of Land, Infrastructure and Transport [15]. Even though the average concentration of formaldehyde for the test pieces with

degradation was below the standard, two out of the three test pieces exceeded the reference value. This indicates that the ongoing degradation of the Shinan wreck could have a significant effect on the concentration of formaldehyde in the exhibition hall. Since formaldehyde produces formic acid as a result of its reaction with the moisture in the air, it can be concluded that other objects in the exhibition hall were possibly affected as well. According to the environmental monitoring conducted for 10 months in 2018, the indoor concentration of formaldehyde in the exhibition hall was $106 \pm 61 \mu g/m^3$ [14]. Based on this environmental monitoring, we can assume that the Shinan wreck is one of the major sources of formaldehyde in the exhibition hall. Therefore, it can be assumed that the acid-degradation on the Shinan wreck plays an important role for the indoor concentration of formaldehyde in the exhibition hall.

It also seems that the degradation of PEG is probably one of the main reasons for the creation of formaldehyde, and that acidic by-products accelerate the degradation of both PEG and wood polymer. Previous studies support the idea that formaldehyde possibly originates from the degradation of PEG. An analytical research conducted by Almkvist and Persson found that an increased level of formic acid accompanied by oxidative degradation of PEG on the Swedish warship, Vasa [16]. There is more research that also supports this hypothesis. After the experiment on aged PEG, Mortensen found that formic acid was detected along with broken down form of the PEG [17]. Since formaldehyde easily oxidizes and forms formic acid, it seems that the formaldehyde emitted from the ship pieces tested were a result of the degradation of PEG.

The result of the bag test showed that the concentration of acetaldehyde was the highest compound among all of the carbonyl compounds for all of the test pieces. Acetaldehyde (3197.7 $\pm$ 1090.5$\mu g/m^3$) had an emission concentration that was about 4 times higher in test pieces that featured degradation in particular, than those shown by the degradation-free test pieces (792.2 $\pm$ 271.4$\mu g/m^3$). This indicates that the acid-degradation had an impact on the emission of acetaldehyde. The level of acetaldehyde in both groups exceeded the environmental standards (50$\mu g/m^3$) established by the Ministry of Land, Infrastructure and Transport [14]. It should also be noted that although the emission of acetaldehyde from the ship pieces tested were extremely high in all the test samples, previous environmental monitoring showed that the level of acetaldehyde in the exhibition hall of the National Maritime Museum was quite low (3.1 $\mu g/m^3$). The reason for this huge difference might be because of the thermal degradation of PEG on the samples tested, as supported by previous studies where acetaldehyde was generated from thermal degradation of ethylene glycol-based materials [18-19]. Therefore, it could be possible that once PEG is degraded by time or acidic substances in archaeological wood, the polymer chains will break down and, when exposed to a high temperature, acetaldehyde is generated in correlation with the thermal degradation of ethylene glycol. Since the test samples were exposed to a temperature of 65℃ for 2 hours in an oven, there is the possibility that acetaldehyde was generated during the pretreatment process. Thus, the concentration of acetaldehyde from the bag test was probably overestimated due to the thermal degradation of PEG during the pretreatment process.

Other carbonyl compounds such as propionaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde, isovaleraldehyde, and valeraldehyde showed higher concentrations in Group Ⅱ than those of Group Ⅰ as represented in table 5. As for the sources of carbonyl compounds from the acid degraded archaeological wood, Almkvist and Persson found that a carboxylic acid end group was observed in correlation with the degradation of PEG in archeological wood [16]. They also found that formic acid, acetic acid, glycolic acid, and oxalic acid were produced, resulting in the oxidative degradation of wood polymers. Since these acidic substances are final products of the reaction, the carbonyl compounds detected from the test pieces were probably due to the oxidative degradation of PEG and wood polymers.

Table 5. Concentrations of Carbonyl compounds of Group I and Group II. (unit: $\mu g/m^3$)

Group Compound	Group Ⅰ			Group Ⅱ		
	S-1	S-2	S-3	S-4	S-5	S-6
Formaldehyde	114.4	68.4	86.4	85.5	217.5	237.8
Acetaldehyde	984.7	910.1	481.8	3248.7	4261.9	2082.6
Propionaldehyde	22.3	21.4	14.9	59.8	68.7	50.4
Crotonaldehyde	7.9	8.0	6.1	21.3	26.2	21.9
Butyraldehyde	21.5	21.0	12.6	76.0	85.7	67.9
Benzaldehyde	8.3	8.8	7.0	10.5	12.4	11.2
Isovaleraldehyde	3.5	3.6	2.3	29.8	40.6	29.4
Valeraldehyde	3.5	3.2	2.1	5.7	5.7	5.3

Sulfur dioxide

For Group Ⅱ featuring degradation, the average emission concentration of sulfur dioxide was 6.021 ± 1.733ppm, which is about two times higher than that (average of 2.911 ± 1.001ppm) shown by the degradation-free Group I. The sulfur in the Shinan wreck is assumed to have been produced as a metabolite of the anaerobic bacteria present in mud under the ocean [20]. As it has been identified already, sulfur in the sediment permeated into the wood and then caused the degradation due to a reaction between PEG, iron compounds, moisture, and oxygen [2]. The air quality monitoring of the exhibition hall conducted in 2018 showed that the concentration of sulfur dioxide was 28.9 ± 36.2ppb [14]. Since there are no other emission sources of sulfur dioxide, it can be assumed that the emission source of sulfur dioxide in the exhibition hall was the Shinan wreck, especially due to the acid-deterioration of the wreck. The acid degradation of the Shinan wreck shows similarity with the Vasa wreck in Sweden and Mary Rose in the UK in which the sulfur in the wood played an important role [3-5, 21, 22]. In addition, a significant amount of sulfur dioxide emissions was also observed in the degradation-free group. These results indicate that sulfur dioxide is being emitted from all parts of the Shinan wreck, even from parts that acid degradation was not detected by simple eye inspection and pH measurements.

Nitrogen oxide

Nitrogen oxide was not detected from the degradation-free group. As for the group where degradation was underway, however, the average emission concentration was 7 ± 1ppm. According to the environmental monitoring of the exhibition hall conducted in 2018, the concentration of nitrogen dioxide was 6.9 ± 2.1ppb [14]. Considering there are no other major emission factors of nitrogen dioxide in the exhibition hall, it can be assumed that the acid degradation of the Shinan wreck is a major emission factor for nitrogen dioxide in the exhibition hall. This was confirmed for the first time that nitrogen oxide was emitted in large quantities from the Shinan wreck through this experiment. Nitrogen oxide is a highly reactive substance that easily forms into nitric acid. Therefore, undertaking de-acidification treatment on the degraded hull of the Shinan wreck is highly recommended to mitigate the emission of nitrogen oxide.

Conclusions

Through a past research project, the acid-degradation of the Shinan wreck was found to have occurred due to a reaction between iron compounds and sulfide ions in a high-humidity environment after PEG treatment. By-products such as sulfur dioxide and sulfuric acid are

generally known to be produced as a result of this reaction. This study found for the first time that large quantities of VOCs, formaldehyde, sulfur dioxide, and nitrogen oxide were produced as byproducts of the acid-degradation of the Shinan wreck.

Most of VOCs emitted from the ship body pieces tested were natural VOCs, aromatic compounds of plants extract such as calamenene, amorpahene-A, junipene, selinane, and etc. Therefore, the characteristics of VOCs are totally different from those that are seen in newly built buildings or construction interior materials. It also seems that VOCs were generated from the Shinan wreck is the result of the degradation of wood polymers. And the acidic by-product created by the acid-degradation symptom probably accelerates the degradation process of wood polymers. In addition, formaldehyde was found to have been emitted in large quantities as byproducts of the degradation, suggesting that attention should be paid to possible damage to cultural assets due to formic acid as a result. The cause of formaldehyde in the Shinan wreck is probably due to the oxidative degradation of PEG and wood polymers. Since formic acid, sulfuric acid, and nitric acid are generally known to be produced when formaldehyde, sulfur dioxide, and nitrogen oxide react with the moisture in the air and are a main cause of material degradation of cultural assets, management through consistent environmental monitoring of substances in the shipwreck gallery is required in order to prevent possible damage to the surrounding cultural heritage assets.

In conclusion, the hypothesis that the main source of formaldehyde, sulfur dioxide, and nitrogen oxide in the exhibition hall was the Shinan wreck, especially due to the acid-degradation is supported by the findings in this study. To mitigate the effects of those harmful substances, de-acidification treatment is necessary to apply for the parts of the Shinan wreck degrade by acid by controlling the humidity in the exhibition hall.

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