

Article

Extraction of Soluble Salts and Iron Sulfides from the Wood of the “Huaguangjiao I” Shipwreck

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Abstract: Shipwreck wood often contains soluble salts and iron sulfides, which pose a threat to its stability. Therefore, desalination treatment must be carried out during protection. In this study, deionized water and ethylene diamine tetraacetic acid disodium salt (EDTA-2Na) solution were used to extract soluble salts and iron sulfides from the 511 wood components of the “Huaguangjiao I” shipwreck. The extraction lasted for 1120 days, during which extraction progress was monitored by measuring the electrical conductivity and iron content of the soaking solution. The results indicated that the extraction experiment reached its endpoint when the conductivity of the soaking solution was maintained at 80~100 $\mu\text{S}/\text{cm}$ and the iron content was maintained at 8~15 mg/L . More than 143.35 kg of iron were extracted from the wood of the “Huaguangjiao I” shipwreck. After extraction, the content of soluble salt ions in the wood were less than 5 $\mu\text{g}/\text{g}$, with an iron content below 5%. The wood has returned to its original color and with a certain degree of degradation. “Huaguangjiao I” was the first large-scale marine shipwreck to complete the desalination treatment of all wooden components. This study provides guidance for the desalination treatment of large-scale wooden shipwrecks.

Keywords: waterlogged wood; extraction; monitoring; conservation; wood composition



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1. Introduction

In 2008, an ancient wooden shipwreck was salvaged from the area of China’s Huaguangjiao island and named “Huaguangjiao I”. The Huaguangjiao shipwreck ruins are located at $111^{\circ}57'\sim 112^{\circ}06'$ E, $16^{\circ}19'\sim 16^{\circ}22'$ N, in the south-central part of the Xisha Islands, China. It belongs to a tropical oceanic monsoon climate. The salinity of the seawater near the shipwreck site is around 34‰, with a depth of 10~25 m. At present, there is no consensus on the reason of the sinking of Huaguangjiao I, and it is speculated that the ship may have been affected by typhoons and reefs on its way to Southeast Asia.

The wreckage of the “Huaguangjiao I” shipwreck measures 17 m long and 7.54 m wide, with three intact cabins remaining. After salvaging, the ship was disassembled into 511 pieces of wooden components and transported to the Hainan Museum for conservation. The original length of most wooden components of the “Huaguangjiao I” shipwreck exceeded 5 m, with the longest piece being 14.4 m. Unfortunately, some longer wooden components were damaged and broke into several parts, including the longest component, which is speculated to have been caused by mechanical impact during sinking and long-term immersion corrosion. The width of the components ranges from 30 cm to 48 cm and the thickness ranges from 2 cm to 5 cm. “Huaguangjiao I” was the first large-scale ancient shipwreck successfully salvaged in Chinese open sea. The ship was mainly used for exporting porcelain and dates back to the Southern Song dynasty (1127–1279 AD). It not only carried precious cargo in ancient times, but also represents the shipbuilding and navigation technology of that period.

Previous studies have shown the presence of various soluble salts and iron sulfides in the wood components of “Huaguangjiao I”, including CaF_2 , CaSO_4 , Fe_2O_3 , MnCO_3 ,

FeCO_3 , FeS_2 , and others [1]. The metal elements that make up these components, such as sulfur, calcium, manganese, etc., mainly came from the marine environment, while the iron mainly came from various household iron products on the ship or components of the ship itself, such as iron pots, ship nails, fasteners, etc. Among them, iron and sulfur elements have the highest content, accounting for 27%~50% and 2%~20% [1], respectively. After the salvage, the soluble salts in the wood will undergo dissolution, crystallization, and re-dissolution reactions to changes in the surrounding environment, which lead to the dissolution and fracture of wood cellulose, further degrading the wood [2]. Iron sulfides can easily oxidize and form acid iron compounds such as melanterite, rozenite, and jarosite. These compounds can acidify the wood matrix, causing discoloration and degradation, resulting in irreversible damage to the wood [3].

For example, for shipwrecks such as the Vasa, Mary Rose, Viking, etc., due to the lack of attention to the issue of iron sulfides at that time, the focus of shipwreck protection was mainly focused on maintaining the dimensional stability of the wood [4–6]. Considering the degradation of the shipwreck's wood, which is prone to wrinkling, deformation, and cracking in the atmospheric environment, PEG was used as a reinforcement agent to fill and reinforce the wood, aiming to achieve good dimensional stability [4]. However, during later exhibitions, due to the lack of desalination treatment, the iron sulfides inside the wood gradually precipitated and oxidized, forming acidic substances on the surface of the wood [7,8]. This acidification posed a risk to the preservation of the shipwreck and compromised its structural integrity.

From 2003 to 2006, researchers carried out the “Preserve Vasa” project. This project involved a systematic study of the sulfur and iron content in the Vasa, the causes of sulfuric acid production, the methods for wood deacidifying and iron extraction, and the stability of PEG in wood. It was found that removing the sulfur and iron compounds inside the wood could solve the acidification of wood completely [9,10]. However, due to the irreversibility of shipwreck protection, complete removal of sulfur and iron compounds from the Vasa shipwreck wood was not possible. Instead, efforts were made to mitigate the process of wood acidification and degradation as much as possible [11,12]. The issue of iron sulfides in shipwreck wood then received widespread attention. As a result, there has been a consensus that in the process of protecting shipwrecks, the extraction of soluble salts and iron sulfides from wood should be prioritized, then the wood should be reinforced to improve its dimensional stability and achieve long-term safe preservation.

The deionized water immersion method is a commonly used method for extracting soluble salts from wood. In order to accelerate the extraction process, methods such as cold-hot water circulation or ultrasonic assistance can be used [13], and the extraction process can be monitored by measuring the electrical conductivity of the soaking solution. Also, the content of soluble salt ions in wood can be regularly tested to help evaluate the extraction effect [13].

There are two ways to remove iron sulfides from wood: sulfur extraction or iron extraction. Some researchers utilized the metabolic action of microorganisms to convert sulfur in wood into soluble sulfides, which can then be extracted from the wood [14]. This method is challenging to operate, inefficient, and difficult to promote for large shipwrecks. Some scholars used electrophoresis to extract iron from the interior of archaeological wood. First, the samples were immersed in conductive salt solutions, such as KNO_3 and EDTA. Then, the samples were wrapped with plastic foam to concentrate the electric field on the wood. The anode and cathode were inserted at both ends of the wood, and the voltage and time were set to extract iron from the wood [15]. The results showed that the extraction effect of this method was not as good as soaking with chelator, and the operation was complex, which was not suitable for large-scale application.

Currently, the most effective method for removing iron sulfides is to soak the wooden relics in a chelator agent [16]. The chelator agent can form stable complexes with iron, increasing the solubility of iron sulfides. This method has high extraction efficiency and minimal side effects, making it suitable for large-scale cultural relics processing [7]. Com-

monly used chelator agents include ethylene diamine tetraacetic acid disodium salt (EDTA-2Na), diethylenetriamine pentaacetic acid (DTPA), and ethylenediimino-bis (2-hydroxy-4-methylphenyl) acetic acid (EDDHMA). Among them, EDTA-2Na allows for treatment under alkaline conditions, with good water solubility and low cost. It has been widely employed in the extraction of iron sulfides from wooden relics and has demonstrated positive results, and the best extraction effect was achieved at a concentration of 10 mmol/L according to previous research [17].

Since research on iron sulfides of shipwrecks has only started in the past decade and primarily focuses on the Vasa and the Mary Rose, there is limited research on the desalination of other archaeological wood [17]. Furthermore, these studies have all focused on small-sized wood. According to the literature reports, the “Huaguangjiao I” is the first large-scale marine shipwreck to undergo comprehensive desalination. Based on this, the desalination method, monitoring method, and effectiveness evaluation method of the wood of the “Huaguangjiao I” shipwreck were introduced, aiming to provide a case for the desalination protection of large-scale marine shipwrecks.

2. Materials and Methods

2.1. Materials

511 Huaguangjiao I wood components were used to extract soluble salts and iron sulfides. The wood species include *Pinus armandii*, *Pinus sylvestris*, *Cupressus funebris* Endl., *Cunninghamia lanceolata* (Lamb.) Hook., *Cinnamomum cassia* Presl, *Pinus massoniana* Lamb., and *Pinus latteri* Mason, with *Pinus massoniana* Lamb. being the main wood species. This was consistent with the common tree species used in ancient shipbuilding, and also in line with the characteristic of using nearby materials for shipbuilding.

EDTA-2Na, CAS number 6381-92-6, was used as the chelator to extract iron sulfides, possessing a purity level of $\geq 99\%$, and a pH range of 4.0–5.0, purchased from Hubei Qifei Pharmaceutical & Chemical Co., Ltd., Tianmen, China. It is important to note that EDTA-2Na has a slight toxicity to humans. If a human is exposed to a large amount of EDTA-2Na for an extended period of time, they may experience symptoms such as redness, stinging, itching, and other skin irritations. However, in this experiment, the staff did not have prolonged or extensive exposure to EDTA-2Na, so it will not cause significant harm. NaOH, CAS number 1310-73-2, was used as an acid-base blending reagent for the soaking solution. It is an industrial-grade substance with a purity level of $\geq 99\%$, and was purchased from Binhua Group Co., Ltd., Binzhou, China.

2.2. Extraction Procedure

The two-step hydrostatic immersion method was used to extract soluble salts and iron sulfides from the shipwreck wood. Two extraction tanks, labeled tank 1 and tank 2 (Figure 1), were built to accommodate all the wooden components of the shipwreck. Each tank had dimensions of 12.76 m $\times$ 5.63 m $\times$ 0.75 m. The volume ratios of wood and solution in tank 1 and tank 2 were approximately 4.2 and 3.9, respectively. In each tank, multiple polypropylene double-layer shelves were installed. These shelves had a size of 3 m (length) $\times$ 0.7 m (width) $\times$ 0.5 m (height) and were used to place the wooden components. To prevent scattering or movement during the extraction process, several smaller wood components of similar size were wrapped and fixed together with polyethylene mesh before being placed on the shelves, while larger wood members were directly placed on the shelves. To ensure proper soaking and prevent overlap, it was necessary to maintain a distance of at least 10 cm between each component.



(a) Tank 1

(b) Tank 2

Figure 1. Extraction tank: (a) Tank 1; (b) Tank 2.

Firstly, deionized water was used as a soaking solution to extract soluble salts from the wood. Then, based on the previous study, a 10 mmol/L EDTA-2Na aqueous solution was used as the soaking solution to extract iron sulfides from the wood [18]. The pH value of the solution was regularly monitored during the soaking process of EDTA-2Na, and a 60% NaOH solution was used to maintain the pH value around 7. The temperature of the soaking solution was not controlled during the soaking process, and the ambient temperature ranged from 15 °C to 35 °C.

According to the preliminary study, using EDTA-2Na solution to soak wooden components with a size of 100 × 25 × 2 cm, the iron content in the solution reached saturation after approximately 40 days [18]. Considering the growth of microorganisms and cost during the extraction process, the extraction time was set to be around 60–65 days. The extraction of soluble salts proceeded as planned. However, during the extraction process of iron sulfides, it was noticed that as the soaking time increased, the solution gradually turned reddish-brown and developed a noticeable odor. Therefore, in the actual operation, the staff determined the replacement time of the soaking solution based on the depth of color, intensity of odor, and holidays. The replacement cycle length was between 30–60 days.

2.3. Monitoring Methods for Extraction Process

2.3.1. Electrical Conductivity of the Solution

During the soluble salts extraction process, the soluble salt ions in wood will gradually migrate into the solution as the soaking time increases. Therefore, the extraction process can be indirectly determined by measuring the electrical conductivity of the solution [15]. The time between two replacements was considered as one cycle. In each cycle, six locations in each extraction tank (Figure 2) were selected as monitoring points, and the electrical conductivity was measured every 7 days to monitor the soluble salt extraction process. Each point was measured three times to obtain an average. The average conductivity values of six monitoring points were considered as the electrical conductivity of the entire extraction tank solution.

The conductivity meter (HannaHI-98303, HANNA, Villafranca Padovana, Italy) used has a measuring range of 0~1999 $\mu\text{S}/\text{cm}$ with an accuracy of $\pm 2\%$ F.S. and a resolution of 1 $\mu\text{S}/\text{cm}$. It is suitable for temperatures ranging from 0 to 50 °C.

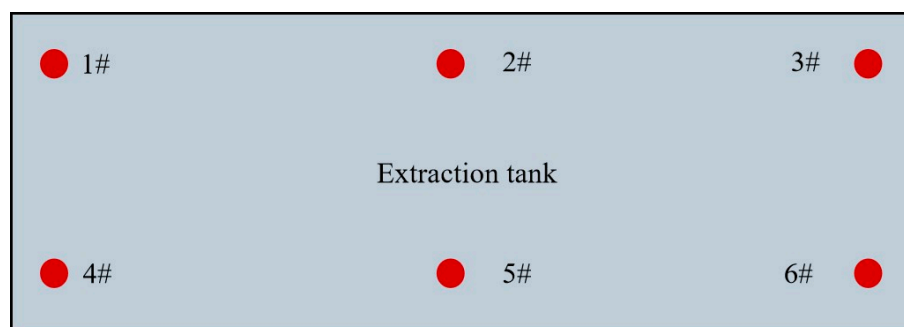


Figure 2. Conductivity monitoring points.

The soluble salt extraction was considered complete when the electrical conductivity of the soaking solution remained constant and no longer increased [3]. In this study, the “Huaguangjiao I” wooden components were immersed for eight cycles, for a total of 520 days.

2.3.2. Iron Content of the Solution

The extraction process of iron sulfides was monitored using the changes of the iron content in the soaking solution. The time between two replacements was considered as one cycle. Within each cycle, the iron content in soaking solution was tested every 10 days to monitor the process of iron sulfide extraction. The distribution of monitoring points was consistent with the above (Figure 2). Each point was measured three times to obtain an average. The average values of six monitoring points were considered as the iron content of the entire extraction tank solution.

The iron content in the soaking solution was measured using a plasma emission spectrometer (IRIS Advantage, Thermo Fisher Scientific, Waltham, MA, USA). The ICP-AES wavelength range is 175~1050 nm, with a carrier gas flow rate of 0.5 L/min, and a generator power of 1.150 W.

The iron sulfide extraction was considered finished when the iron content of the soaking solution was maintained at a certain level and no longer increased [3]. In this study, the wooden components of “Huaguangjiao I” were immersed for 18 cycles, totaling 600 days.

2.4. Evaluation Methods for Extraction Effect

To evaluate the extraction effect of wood, five wood components (Table 1) from different shelf positions in two extraction tanks were chosen as monitoring samples. Three monitoring areas measuring 50 mm × 50 mm were randomly selected on each monitoring samples, and a wood strip measuring 20 mm × 7 mm × 7 mm was drilled using a growth cone in each monitoring area before and after extraction. These wood strips were then dried and ground into 100 mesh wood powder for further use.

Table 1. Description of monitoring samples.

Samples	Extraction Tank	Shelf Layer	Sample Size (mm)	Wood Species	Sampling Position
25#	No. 1	2	1870 × 65 × 300	<i>Pinus massoniana</i> Lamb.	Northeast of the hull
96#	No. 1	1	620 × 350 × 50	<i>Pinus massoniana</i> Lamb.	The position is not sure
319#	No. 2	2	4590 × 110 × 45	<i>Pinus massoniana</i> Lamb.	The third layer of the hull
383#	No. 2	1	690 × 290 × 35	<i>Pinus massoniana</i> Lamb.	The fourth layer of the hull
488#	No. 2	2	2380 × 245 × 45	<i>Pinus massoniana</i> Lamb.	The fifth layer of the hull

2.4.1. Soluble Salt Ions in Wood

0.4 g of wood powder were weighed and placed in a centrifuge tube, then 10 mL of deionized water was added and stirred evenly. Then the mixture liquid was sonicated for

10 min and left to stand for 48 h. the upper clear liquid was collected and filtered, then ion chromatography (ICS-2000) was used to determine the Cl^- , SO_4^{2-} , K^+ , Ca^{2+} , Na^+ , and Mg^{2+} in the liquid. The average of three tests per sample was taken.

The testing conditions for cations were as follows: Ion Pac CS12A cation exchange column (4 mm $\times$ 250 mm), CG12A ion protection column (4 mm $\times$ 50 mm). The H_2SO_4 with a concentration of 0.70 mmol/L was used as the mobile phase, with a flow velocity of 1.0 mL/min and injection volume of 20 μL .

The testing conditions for anions were as follows: Ion Pac AS19 anion exchange column (4 mm $\times$ 250 mm), Ion Pac AG19 ion protection column (4 mm $\times$ 50 mm). The Na_2CO_3 with a concentration of 0.35 mmol/L was used as the mobile phase, with a flow velocity of 1.0 mL/min and injection volume of 20 μL .

2.4.2. Sulfur and Iron Contents in Wood

10 mg of wood powder were weighed and placed in a polytetrafluoroethylene crucible. Then, 0.75 mL of nitric acid and 0.25 mL of hydrochloric acid were added as digestion solutions. After being well mixed with the digestion solution, the samples were placed in the microwave digestion instrument (Ultra WAVE ECR, Milestone, Sorisole, Bergamo, Italy) to digest at 260 $^\circ\text{C}$. After digestion, the solution was cooled to room temperature and 3% nitric acid was added to reach a volume of 20 mL. The solution was filtered, and then the sulfur and iron content were tested using a plasma emission spectrometer (Prodigy 7, Lehman, PA, USA). The average of three tests was taken for each sample. The detection limit of this instrument ranges from $\mu\text{g/L}$ to $\mu\text{g/mL}$, with a wavelength range from 165 nm to 1100 nm.

2.4.3. Wood Color

The CIE $L^* a^* b^*$ system was commonly used to measure changes in wood color. The L^* represented brightness, with $L^* = 0$ indicating black and $L^* = 100$ indicating white. The a^* represented the red–green index, where negative values indicated green and positive values indicated magenta. The b^* represented the yellow–blue index, with negative values indicating blue and positive values indicating yellow [19]. The overall color change of wood can be expressed as the total color difference ΔE ($\Delta E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$) [20].

When testing the wood color, the samples were taken out from the tanks and the surface moisture was wiped clean. Then, a handheld colorimeter (blue tooth CM-700d, Konica Minolta, Tokyo, Japan) was used to test the L^* , a^* , and b^* values of the monitoring area on the monitoring samples' surface. The color test of samples was carried out at the tangential section, as the wood components of the “Huaguangjiao I” shipwreck were mainly chord-cut boards, and the five wood monitoring samples were also chord-cut boards. Three test points were selected for each wood, and each test was at the same location. The test was conducted every six months, and the average of three measurements was taken each time.

2.4.4. Wood Composition

Take the above wood powder to determine the ash, holocellulose, and lignin content of the wood samples before and after extraction. According to standard regulations, the average of two measurements was taken each time.

The content of ash was determined according to Chinese national standard GB/T 2677.3-93 [21]. The wood powder samples were dried and weighed (around 1.0000 g), and then placed into well-desiccated porcelain crucibles and then in a muffle furnace set at 550 $^\circ\text{C}$ to 600 $^\circ\text{C}$ for 3 h. The ash content was determined gravimetrically. The calculation formula for ash content was as follows:

$$x_A = \frac{m_2 - m_1}{m} \times 100 \quad (1)$$

x_A is the content of ash (%), m_1 is the weight of sintered glass crucible (g), m_2 is the weight of sintered glass crucible containing ash (g), and m is the weight of wood powder (g).

The content of hollocellulose was determined according to the Chinese national standard GB/T 2677.10-1995 [22]. Approximately 2.0000 g of extractive-free wood powder was placed in an Erlenmeyer flask. Then, 65 mL of water and 0.6 g of a sodium chlorite (NaClO_2) aqueous solution were added and 0.5 mL of glacial acetic acid was slowly incorporated under stirring. After being covered with a small, inverted Erlenmeyer flask, the mixture was heated to 90 °C. After 2 h, the solid residue was filtered at room temperature in a sintered glass crucible, washed with distilled water and oven dried.

In order to better compare the changes in the wood components of hollocellulose and lignin before and after extraction, the influence of ash was removed when calculating the content of cellulose and lignin. The results were normalized for the carbon-based materials.

The calculation formula for test content of hollocellulose was as follows:

$$x_{h0} = \frac{m_h - m_A}{m} \times 100 \quad (2)$$

The calculation formula of normalized content of hollocellulose was as follows:

$$x_{h1} = \frac{m_h - m_A}{m - m_A} \times 100 \quad (3)$$

x_{h0} is the test content of hollocellulose (%), x_{h1} is the normalized content of hollocellulose (%), m_h is the weight of hollocellulose (g), m_A is the weight of ash (g), and m is the weight of wood powder (g).

The content of lignin was determined according to Chinese national standard GB/T 2677.8-94 [23]. First, 2.0000 g of wood powder was weighed. Then, the sample was extracted with 72% H_2SO_4 solutions at 18–25 °C for 4 h. Then, the solid residue was filtered at room temperature and washed with distilled water and oven dried.

The calculation formula of test content of lignin was as follows:

$$x_{L0} = \frac{m_L - m_A}{m} \times 100 \quad (4)$$

The calculation formula of normalized content of lignin was as follows:

$$x_{L1} = \frac{m_L - m_A}{m - m_A} \times 100 \quad (5)$$

x_{L0} is the test content of lignin (%), x_{L1} is the normalized content of lignin (%), m_L is the weight of lignin (g), m_A is the weight of ash (g), and m is the weight of wood powder (g).

3. Results and Discussion

3.1. Extraction of Soluble Salts

Figure 3 shows the changes in electrical conductivity of the soaking solution in two extraction tanks during the extraction of soluble salts, which followed a similar trend for tanks 1 and 2. The time between the two adjacent dotted lines represents one cycle. Within each cycle, as the soaking time prolongs, the conductivity gradually increases, indicating the migration of soluble salts from the wood into the solution. Furthermore, in each subsequent cycle, the peak value of electrical conductivity continues to decrease, indicating a reduction in the total amount of soluble salts in the wood.

The increasing trend of electrical conductivity during cycles 1~8 was analyzed using linear regression. The results showed that the slope of the conductivity change line of cycles 1~8 was 0.89, 1.15, 1.14, 0.87, 0.86, 0.72, 0.55, and 0.32, respectively, which increased first and then decreased. This change can be attributed to the structure and composition of the shipwreck wood. The inner pores of shipwreck wood were filled with impurities such as putrefaction and inorganic matter [24]. As the soaking time increased, these impurities were gradually extracted, leading to the opening of fluid channels inside the wood [25]. Consequently, the extraction speed of soluble salts increased, particularly the soluble salt in large pores such as vessels and fibers began to be removed rapidly. In the late stage of

the extraction, most of the soluble salts in the macropores were eliminated, turning to the removal of soluble salts in small pores such as the intercellular layer and pits, which have narrow fluid channels and lower soluble salt content, resulting in a slower rate of soluble salt extraction [26].

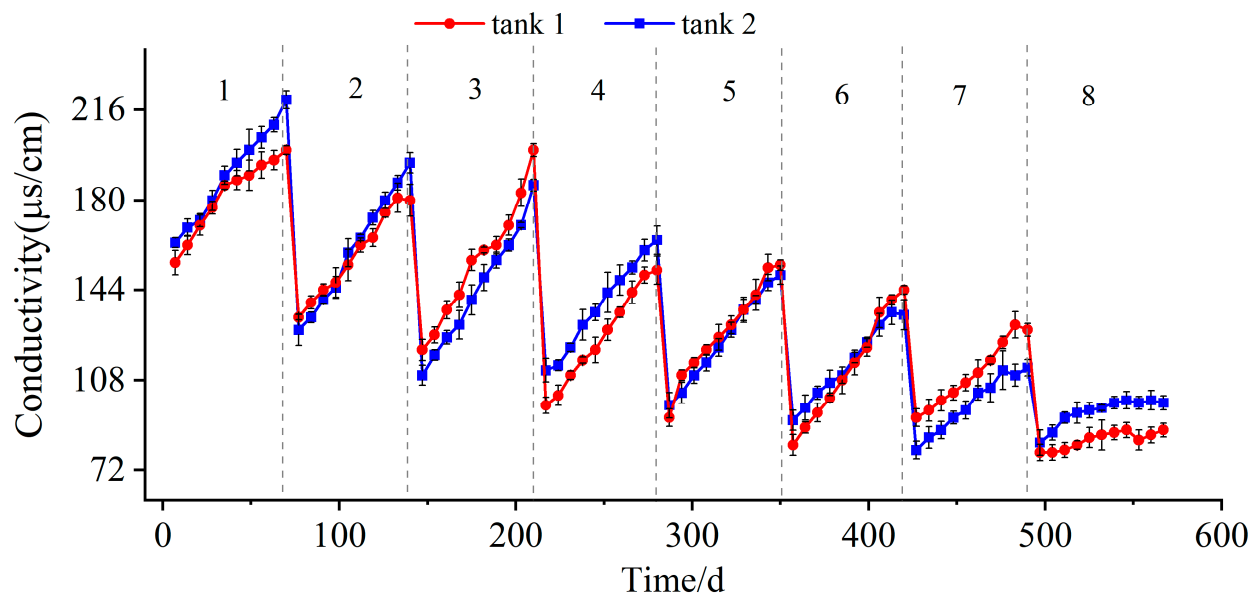


Figure 3. Electrical conductivity of the soaking solution.

Therefore, the electrical conductivity of the solution no longer significantly increased with time and stabilized around 80–100 $\mu\text{s}/\text{cm}$ in the eighth cycle, indicating that the soluble salt ions in the wood were no longer migrating noticeably. Comparing this conductivity with that of the cold water extract of pine wood, which ranges from 60–180 $\mu\text{s}/\text{cm}$ [27,28], it can be concluded that most of the soluble salts in the wood had been successfully removed, and the extraction of iron sulfides could be implemented.

3.2. Extraction of Iron Sulfides

Figure 4 shows the change of iron content in two extraction tanks. The time between the two adjacent dotted lines represents one cycle. The changes in the content of sulfur iron compounds within each cycle and throughout the entire extraction process are similar to those of soluble salts extraction process. From cycles 1–12, the iron content increased rapidly with prolonged soaking time in each cycle. However, from cycles 13–18, the iron content of the soaking solution no longer significantly increased with time and remained stable within the range of 8 to 15 mg/L, indicating the successful extraction of iron sulfides from the wood.

Previous studies have shown that iron sulfides in wood were mainly distributed on the surface and in large pores such as vessels and tracheids, with a smaller amount found in small pores like the intercellular layer and pits. Moreover, some of them are bound to lignin in the intercellular layer or cell wall [7,29]. For cycle 1, at the initial stage, the iron sulfides on the wood surface began to be removed, accompanied by slow penetration of soaking solution into the interior of the wood, resulting in a faster extraction speed. For cycles 2–11, the soaking solution penetrated into large pores of the wood, such as vessels and tracheids. These areas contained a high content of iron sulfides and wide fluid channels, which initiated the rapid extraction stage [25].

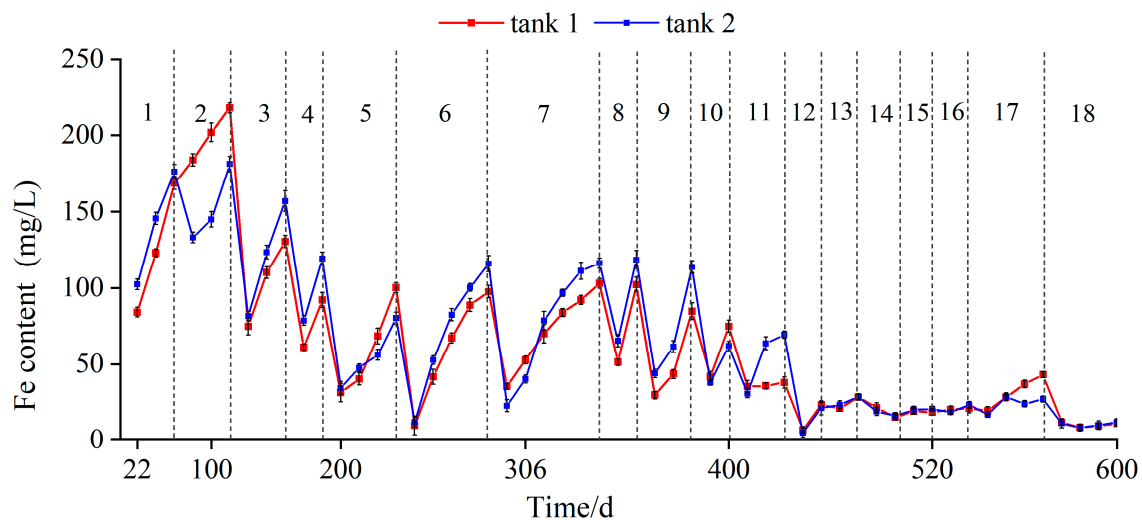


Figure 4. Iron content of the soaking solution.

During cycles 12~18, the extraction rate of iron sulfides decreased, because the extraction primarily occurred in small pores such as the intercellular layer and pits, where the content of iron sulfides was low and the fluid channels were narrow [7,29], making the extraction more challenging. However, these iron sulfides in wood did not easily migrate and caused minimal harm for later protection [3]. Therefore, it can be considered that the extraction of iron sulfides from the wood was completed.

Based on the maximum iron content of the soaking solution in the extraction tank for each cycle, the total amount of iron removed from the soaking solution could be approximately calculated, and the calculation formula was as follows:

$$\sum_{1}^{18} M = W \times V \quad (6)$$

M is the total amount of iron removed in each cycle (kg), W is the maximum iron content (mg/L) of each cycle, and V is the volume of the soaking solution (L).

After calculation, a total of 74.90 kg of iron were removed from the tank 1, and 68.45 kg of iron were removed from the tank 2. This means that a total of 143.35 kg of iron were removed from the wooden components of the “Huaguangjiao I” shipwreck. However, due to experimental limitations, the iron in the shipwreck wood was not completely removed. Therefore, the actual iron content in the wood should be greater than 143.35 kg.

3.3. Effects of Desalination on the Wood

3.3.1. Soluble Salt Content

In order to accurately determine the extraction effect of soluble salt in wood, the main soluble salt ions in shipwreck wood monitoring samples were measured before, at 200 days, and after the experiment. The average results are shown in Table 2. According to the table, all five monitoring samples had the same types of soluble salt ions, including Ca^{2+} , SO_4^{2-} , Na^+ , Mg^{2+} , Cl^- , and K^+ . The initial contents of Ca^{2+} , SO_4^{2-} , and Na^+ were over 12 $\mu\text{g/g}$, while those of Mg^{2+} , Cl^- , and K^+ were below 5 $\mu\text{g/g}$.

After soaking in deionized water for eight cycles, the trend of the change of soluble salt ions in the five monitoring samples remained consistent. The contents of Ca^{2+} , SO_4^{2-} , and Na^+ decreased to less than 5 $\mu\text{g/g}$, achieving an extraction rate of over 70%. The contents of Mg^{2+} , Cl^- , and K^+ were almost undetectable. This confirmed that most of the soluble salt have been removed from the wood components of the “Huaguangjiao I” shipwreck, which corresponds to the results of conductivity detection of the soaking solution.

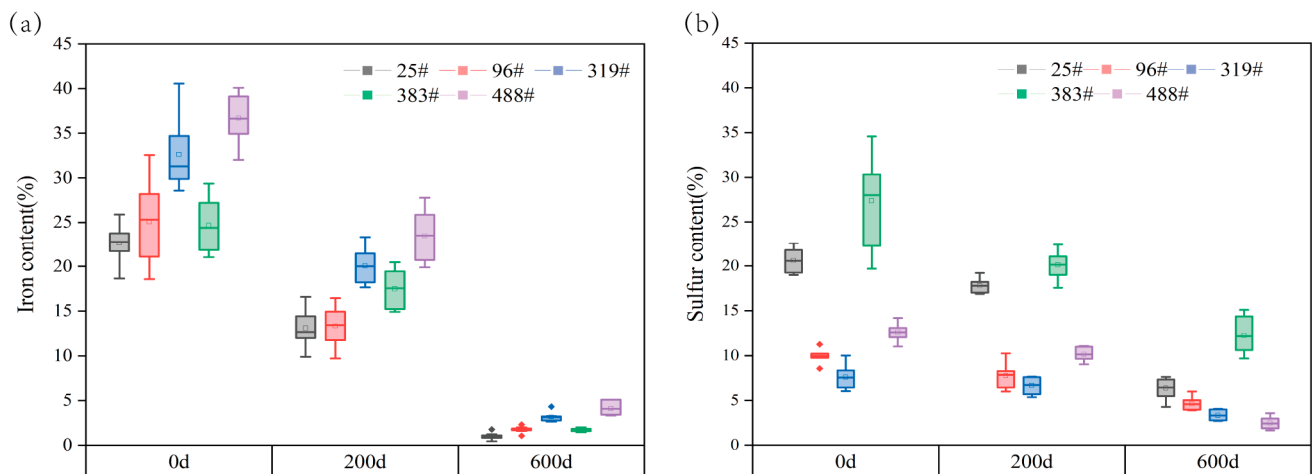
Table 2. The content of soluble salt ions in wood ($\mu\text{g/g}$).

Samples	Time	Ca^{2+}	SO_4^{2-}	Na^+	Mg^{2+}	Cl^-	K^+
25#	0 d	12.59 ¹ (4.77)	24.65 (6.30)	47.33 (2.48)	1.00 (10.35)	1.62 (7.68)	3.91 (3.56)
	200 d	10.65 (7.58)	6.92 (5.92)	30.46 (3.05)	0.83 (8.62)	1.48 (9.66)	1.81 (9.56)
	520 d	0.54 (7.65)	0.98 (10.62)	13.70 (4.62)	0.21 (7.66)	0.33 (5.68)	0.09 (11.08)
96#	0 d	20.58 (3.51)	32.2 (5.03)	28.95 (5.34)	2.09 (5.89)	2.54 (5.90)	4.05 (3.29)
	200 d	15.25 (9.21)	19.65 (5.98)	20.46 (11.28)	1.65 (6.45)	1.85 (10.95)	2.59 (3.99)
	520 d	1.65 (6.98)	0.12 (6.59)	4.42 (8.23)	0.11 (5.46)	0.28 (5.68)	0.04 (10.58)
319#	0 d	35.66 (8.21)	25.12 (2.34)	19.58 (6.56)	2.85 (9.64)	1.49 (13.24)	2.89 (3.56)
	200 d	25.16 (9.60)	20.01 (4.62)	13.65 (3.95)	2.09 (8.25)	1.03 (8.36)	1.69 (6.29)
	520 d	1.28 (5.88)	1.67 (4.88)	1.93 (5.44)	0.05 (11.20)	0.28 (9.24)	0.07 (5.89)
383#	0 d	18.95 (4.65)	19.28 (6.50)	40.12 (2.38)	0.98 (8.03)	3.02 (13.25)	5.02 (10.28)
	200 d	10.36 (5.02)	11.28 (5.02)	25.39 (7.62)	0.54 (5.98)	2.18 (15.68)	3.59 (9.35)
	520 d	1.64 (9.06)	0.88 (9.16)	0.50 (8.06)	0.08 (9.68)	0.29 (3.28)	0.10 (8.66)
488#	0 d	21.08 (7.06)	32.05 (3.19)	21.08 (7.30)	1.06 (10.28)	2.18 (12.62)	3.50 (8.63)
	200 d	16.81 (4.67)	25.28 (4.92)	16.37 (4.35)	0.78 (6.89)	1.85 (11.35)	2.56 (11.25)
	520 d	2.01 (3.59)	1.59 (7.77)	1.92 (9.21)	0.05 (9.76)	0.31 (6.87)	0.07 (13.64)

¹ The data present average values of samples (coefficient of variation %).

3.3.2. Iron and Sulfur Contents

To accurately assess the extraction efficiency of iron sulfides in wood, the iron and sulfur content in the monitoring samples were measured before, at 200 days, and after the experiment (Figure 5). The initial content of iron and sulfur varied among different monitoring samples, ranging from 20% to 37% (Figure 5a) and 8% to 27% (Figure 5b), respectively. These results indicate that the distribution of iron and sulfur in wooden components at different shipwreck positions is uneven, and the concentration of iron is usually higher than that of sulfur.

**Figure 5.** Changes of sulfur and iron contents in wood, (a) iron (b) sulfur.

The iron and sulfur contents in the monitoring samples consistently decreased with an increase in soaking time. After extraction, the iron content in all five monitoring samples was below 5%, with an extraction rate of over 95% (Table 3). The sulfur content ranged from 3% to 15%, with an extraction rate of 52%~80% (Table 3). The sulfur extraction rate was lower than that of iron due to the poor binding ability between sulfur and EDTA-2Na, and some sulfur was bound with lignin in the intercellular layer or cell wall, making it “non-extractable sulfur” [7,29].

Table 3. Extraction rate of sulfur and iron in wood (%).

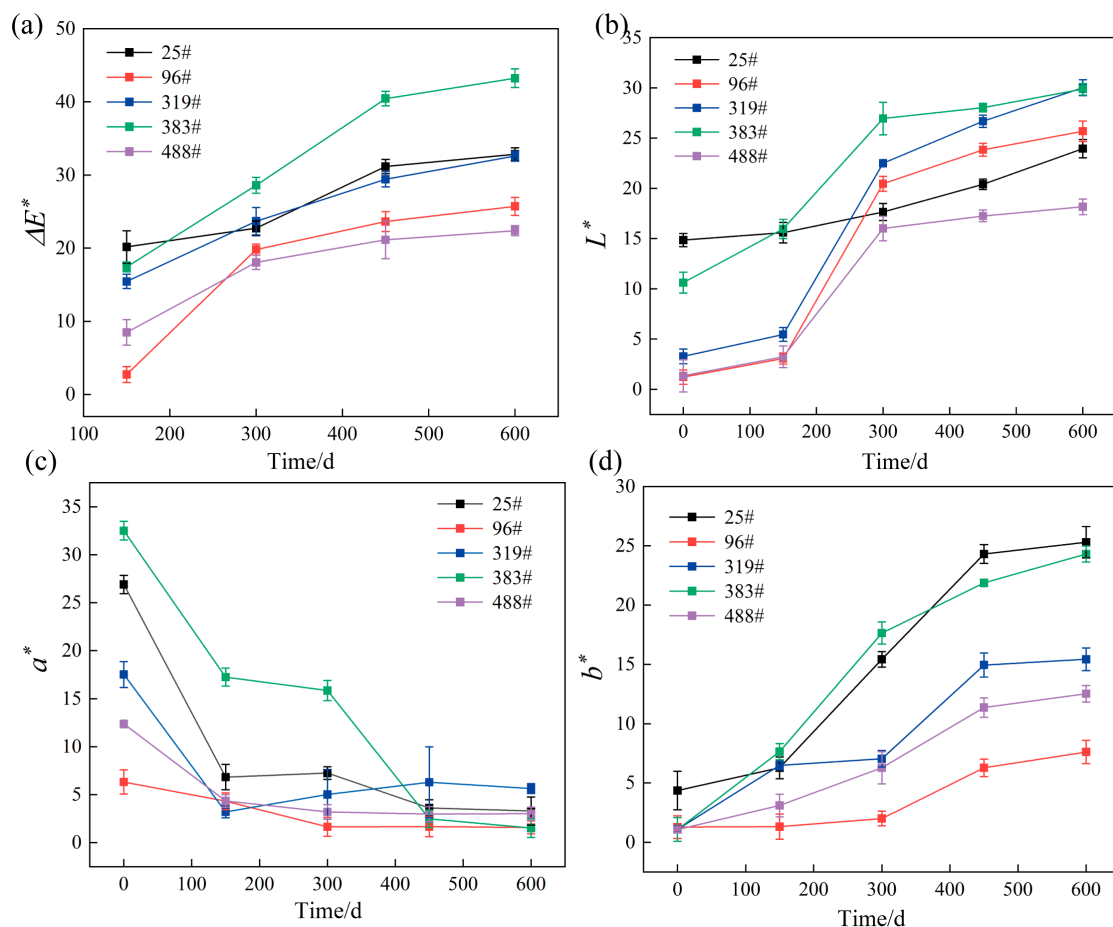
	25#	96#	319#	383#	488#
Iron	99.15 ¹ (2.36)	99.32 (2.02)	99.03 (1.84)	98.91 (1.38)	99.16 (2.01)
Sulfur	68.66 (8.77)	52.39 (13.51)	53.05 (10.19)	55.55 (7.24)	79.94 (8.35)

¹ The data present average values of samples (coefficient of variation %).

3.3.3. Wood Color

Several factors, such as temperature, light exposure, aging time, etc., can affect the color of wood [30,31]. Fundamentally, these external factors change the color of wood by altering its chemical composition or structural changes, such as lignin and sedimentation, which are the main determinants of wood color [32–34]. Previous study revealed that the wood species used for the “Huaguangjiao I” shipwreck mainly belong to the *Pinaceae* family. Healthy pine wood exhibits a light yellow color, while the moisture content exceeds 100%, with L^* values ranging from 20 to 40, a^* values ranging from 4 to 16, and b^* values ranging from 10 to 35 [35]. The presence of iron sulfides in the wood caused it turn to dark red or brown [36].

Figure 6a–d shows the changes in ΔE^* , L^* , a^* , and b^* values during the iron sulfide extraction process of the monitoring samples. It can be observed that all samples exhibited a similar trend: L^* values gradually increased, a^* values gradually decreased, and b^* values gradually increased. This suggests an increase in brightness, a decrease in the red tone, and an increase in the yellow tone, indicating that the wood has returned to its original color.

**Figure 6.** Changes in wood color: (a) ΔE^* (b) L^* (c) a^* (d) b^* .

The ΔE^* values of the five monitoring samples after extraction were 32.84, 25.72, 32.58, 43.24, and 22.40, respectively. All of these values were higher than 22, indicating

a significant change in the color. Additionally, the ΔE^* value of the monitoring samples showed a notable increase during the first 450 days of the extraction process and stabilized at a later time (Figure 6a). This trend was consistent with the changes in iron concentration in the soaking solution (Figure 5). These findings demonstrated that the ΔE^* value could reflect the iron sulfide extraction process, and the wood color change can serve as an indicator for evaluating the extraction process of iron sulfides.

3.3.4. Chemical Composition

Due to the long extraction time, the wood may undergo hydrolysis [3], which affects its composition. Therefore, the holocellulose, lignin, and ash content of five monitoring samples were determined before and after extraction. Table 4 shows that the holocellulose content of wood samples ranged from 33% to 53% before treatment, which was lower than that of healthy wood. The lignin content ranged from 43% to 62%, being generally consistent with healthy wood. The ash content ranged from 39% to 56%, significantly higher than healthy wood [37,38]. The wood from the Vasa had a holocellulose content of 70.5%, a lignin content of 26.6%, and an ash content of 2.6%. The ancient Chinese sunken ship Luoyang I had a holocellulose content ranging from 32% to 38% and a lignin content ranging from 53% to 57%. When comparing these two shipwrecks, it was found that the wood from the “Huaguangjiao I” shipwreck has undergone severe degradation and contains a significant number of inorganic substances [1,24].

Table 4. Chemical components of wood before and after extraction (wt%).

Samples	Extraction Status	Holocellulose	Lignin	Ash
25#	before	52.56 ¹ (5.67)	43.42 (10.24)	55.33 (7.62)
	after	36.43 (6.42)	64.66 (8.99)	2.11 (3.15)
96#	before	49.50 (7.21)	61.72 (5.68)	39.44 (6.84)
	after	35.36 (6.88)	53.53 (4.38)	2.92 (2.45)
319#	before	41.95 (8.25)	49.02 (9.68)	49.21 (4.77)
	after	27.77 (6.11)	49.09 (6.44)	7.28 (4.28)
383#	before	50.44 (4.28)	47.83 (5.97)	53.09 (3.65)
	after	38.03 (9.24)	57.53 (8.23)	6.01 (6.68)
488#	before	48.62 (7.16)	43.18 (4.59)	46.67 (9.55)
	after	33.07 (5.42)	41.85 (6.48)	4.39 (5.34)
Vasa [39]	before	70.5	26.6	2.9
Luoyang I [40]	before	32–38	53–57	-

¹ The data present average values of samples (coefficient of variation %).

After extraction, the holocellulose content ranged from 27% to 39%, the lignin content ranged from 41% to 65%, and the ash content ranged from 2% to 8%. The holocellulose content decreased by about 25% to 32%, compared to before desalination. Previous studies have shown that a decrease in the degree of polymerization for cellulose occurs in the presence of chelators under weakly acidic conditions [31]. It has been demonstrated that the complex formed by the chelator and iron may promote oxidative reactions [17]. Therefore, the holocellulose was degraded. Overall, the change in lignin content before and after desalination is not significant, indicating that lignin is relatively stable. The ash content has significantly decreased, with a decrease rate of 85%~96%, indicating a significant desalination effect on the wood. Based on the above analysis, it can be concluded that EDTA-2Na can cause a certain degree of degradation of holocellulose in wood. In the future, it is still necessary to search for safer and more effective desalination reagents.

4. Conclusions

“Huaguangjiao I” was the first large-scale marine shipwreck to complete the desalination treatment of all wooden components. In this study, the deionized water and EDTA-2Na solution was used to extract soluble salts and iron sulfides from the 511 wood components of the “Huaguangjiao I” shipwreck. The extraction lasted for 1120 days. The results are as follows:

- (1) The extraction process can be monitored using the electric conductivity and iron content of the soaking solution. When these two values are stable in a lower range and do not obviously change with time, the extraction process is considered to be finished. In this study, at the end of extraction, the electrical conductivity of the solution stabilized at 80–100 $\mu\text{S}/\text{cm}$, and the iron content ranged from 8 to 15 mg/L .
- (2) The extraction effect of shipwreck wood can be evaluated by observing the change of soluble salt ion content, iron content, color, and composition of the wood before and after extraction. In this study, after the extraction treatment, the various kinds of soluble salt ion content in the shipwreck wood were all below 5 $\mu\text{g}/\text{g}$, the iron content was below 5%, and the wood returned to its original color with a certain degree of degradation.
- (3) The two-step hydrostatic immersion method using deionized water and EDTA-2Na as the extraction solution has a good effect on removing soluble salts and iron sulfides from large-scale shipwreck wood. But this method requires a long time, and EDTA-2Na will cause a certain degree of degradation of wood. It is recommended to seek safer and more effective desalination methods in the future.

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