Scientific analysis and conservation of porcelain recovered from the Nanhai I in the South China Sea

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Abstract

The Nanhai I is a merchant ship which sank in the South China Sea 800 years ago while transporting different kinds of precious porcelain and metal work. The Nanhai shipwreck is 30 m long wooden vessel lay in 25 m of water and was covered by fine sediment. Most of the porcelain artefacts are discs, bowls, vases and pots. Some of them were covered by thick encrustations. In this research, X-ray fluorescence energy dispersive X-ray (XRF-EDX) analysis and ion chromatography (IC) were employed to investigate the contaminants in these porcelains. Distilled water and alternating hot and cold cleaning were used to remove the harmful salts. Conductivity meter and ion chromatography were used to monitor the desalination processes. Based on these results, an appropriate method was selected to desalinate the porcelain from the Nanhai I shipwreck.

Key words: Nanhai I shipwreck, Porcelain, Ion chromatography, XRF, EDX

Introduction

The Nanhai I was a Song Dynasty shipwreck located south of Dong Ping harbor, Yangjiang City, Guangdong Province, China. It was the first shipwreck excavated in China. The Nanhai I is 30.4 m long, 9.8 m wide and 4 m high (not including the mast) and has an estimated tonnage of 600. In 1987, a British marine exploration company found an ancient shipwreck from The Honorable East India Company, which was loaded with 6 cases of silver and 385.5 tons of fine ingots. In August 1987, the British Company applied to the State Administration of Cultural Heritage of China to salvage the shipwreck. Permission was granted and the salvage plan was carried out as a UK-China co-operative project. During this salvage project another ancient Chinese shipwreck site was located. It was named the Nanhai I. Since the discovery, the shipwreck site has been thoroughly investigated by underwater archaeologists. In 2007, the ship was successfully salvaged in strict accordance with underwater archaeology standards and placed in the “Crystal Palace” of the Maritime Silk-Road Museum of Guangdong. This work was innovative in the history of world underwater archaeology. According to the archaeological investigations conducted over the years and the results of two test excavations, the Nanhai I was loaded with 6000-8000 artefacts, the majority being porcelain. Most of the porcelain came from kilns in Zhejiang Longquan, Fujian Dehua and Jiangxi Jingdezhen. There were over 30 different kinds of porcelain identified; some of them could be classified as Country-level and secondary level based on their estimated value. Many examples had a strong Arabic style, which were identified as the “overseas processing orders” manufactured during the Song Dynasty. In addition, there were some gold items, lacquer-ware and metal artefacts on site.

Some of the artefacts had suffered from prolonged seawater immersion and had been adversely affected by the calcareous cement formed by marine organisms and burial in the seabed for an extended period of time. These concretions incorporated many artefacts forming conglomerations of varying sizes (Wei, 2011). After excavation and recovery, due to changes in temperature and humidity, these concretions caused physical damage to the metal or porcelain artefacts incorporated in the conglomerations (Wei, 2012). Meanwhile, because of the high salt environment of the sea water, the porcelain contained high levels of salt. With changes in the local environment, dissolution and crystallization of the salts occurred causing spalling of the glazes. Therefore, it was extremely important that a procedure to safely extract the cultural relics from the concretions and desalinate the artefacts was found urgently. In this research, XRF-EDX analysis and IC were employed to investigate the contaminants in these porcelains. Based on the results from these analyses suitable chemicals were selected to remove the concretions. Distilled water and alternating hot and cold cleaning were used to remove the harmful salts. Conductivity meter and ion chromatographies were used to monitor the desalination processes. Based on these results, an appropriate method was selected to desalinate the porcelain from the Nanhai I shipwreck.

Composition and soluble salt analysis

Samples description

Ten pieces of porcelain recovered from the Nanhai I were selected for the test analyses. The fragments chosen represent porcelain manufactured at the Jingdezhen Hutian, Dehua, Yaozhou and Cizao kilns from the Southern Song Dynasty and include bluish white porcelain, celadon, brown porcelain and many other varieties (Fig. 1 and Table 1).

Instruments and Testing

Prior to the desalination experiments, XRF-EDX and IC were used to characterize the chemical elements and ion concentrations in the porcelain samples recovered from the Nanhai I shipwreck. The conductivity meter and IC were used to monitor the desalination process.

Constituent testing– XRF-EDX

SHIMADZU EDX-800HS, XRF, Rhodium target (Rh), voltage: Ti-U 50kV; Na-Sc 15kV, the analyses were performed under vacuum for 200 seconds. The results are shown in Table 2-1.

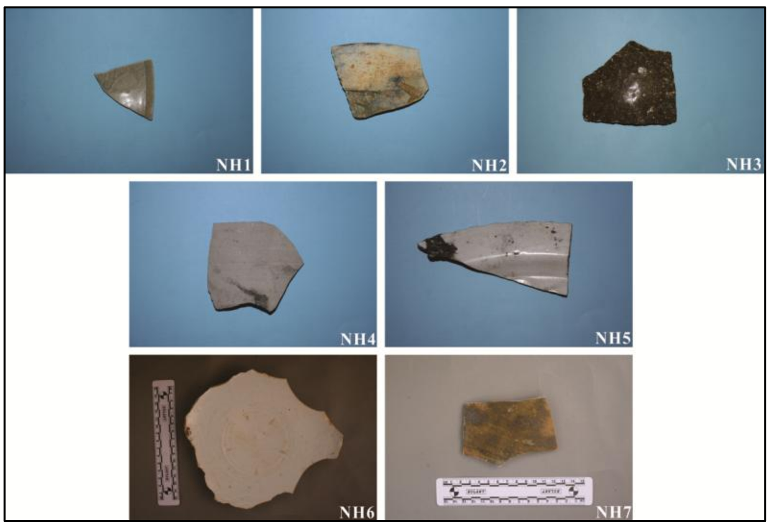

Fig. 1: Images of the ten porcelain samples recovered from the Nanhai I.: (L. Naisheng).

Soluble salts testing – IC

To extract the soluble salts from the ceramics, more than 5g of each sample, normally a powder, was mixed with 50 ml of de-ionized water in a 50 ml volumetric flask for more than 24 hours. The chromatograms were recorded with a Shimadzu SCL-10A ion chromatograph. Anions were analysed using a Shim-pack IC-SA3 (G) pre-column, a Shim-pack IC-SA3 column and an Anion Cartridge Suppressor; cations were analysed using a Shim-pack IC-SC3 (G) pre-column, a Shim-pack IC-SC3 column and a Cation Cartridge Suppressor. A Shimadzu CDD-10Asp conductivity detector and a Shimadzu LC Solution workstation were also used. The volume introduced into the injection valve of the instrument was normally 100 µl and the loop volume was 60 µl. Automatic Science Instrument (Tianjin) F filters (0.22 µm-13 mm) were used to remove solid particles. The results are listed in Table 2-2.

Conductivity meter

The conductivity meter was a portable HANNA HI8733 model, multi-range conductivity/TDS meter with a built-in temperature sensor connected to a HI76302W four ring conductivity electrode. The temperature coefficient compensation is 2.5%/°C and the results of the desalination experiments are shown in Table 2 and 3 and Figs 3 and 4.

Desalination of the porcelain

Desalination methods

The extent of preservation and the composition of the porcelain must be taken into consideration when interpreting the results of the desalination experiments. The number of porcelain artefacts recovered from the Nanhai I was enormous and there were many intact, unbroken objects. So it was decided to experiment with two solutions: 1. a static de-ionized water infusion at room temperature (25°C) and 2 heat the static de-ionized water (50°C) to accelerate the desalination process. The porcelain samples NH1-NH5 were used in this first experiment to select the most appropriate desalination method. Two similar sized pieces of ceramic were cut off from each porcelain sample (NH1-NH5) and weighed accurately. One sub-sample was placed in the static de-ionized water at room temperature (200ml) and the other sub-section placed in the heated de-ionized water solution (200ml). These latter sub-samples were heated in a water bath to 50°C for 8 hours each day and then allowed to stand static for the rest of the time (Fig.

Fig. 2: The desalination experiments for the porcelain samples NH1-NH5.: (L. Naisheng).

2). After 24 hours all solutions were changed. After each change the solutions was measured using the conductivity meter and ion chromatography for a total of 21 days. The solutions were heated for 8 hours every day for 21 days. The results of the desalination experiments for NH1-NH5 are shown in (Fig. 3).

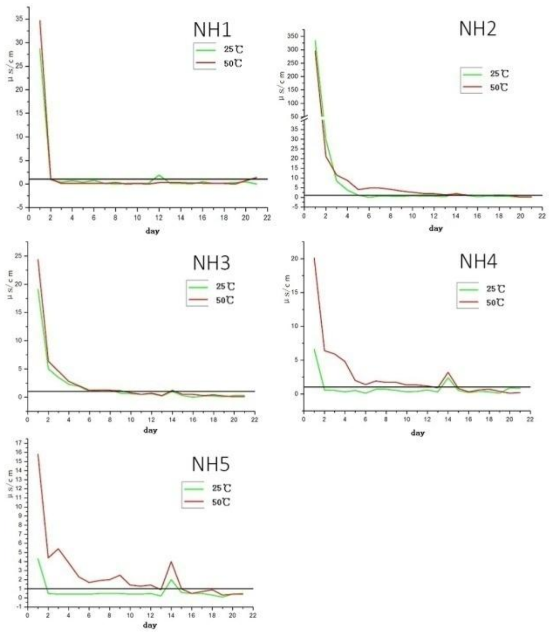

Fig. 3: The daily variation in conductivity of the desalination solution for NH1~NH5.: (L. Naisheng).

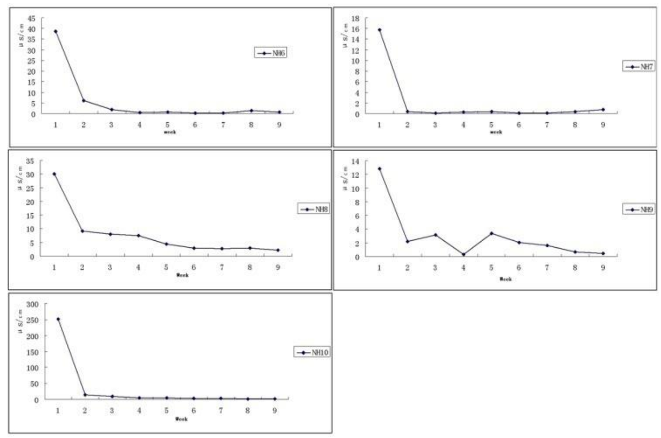

Fig. 4: The weekly variation in conductivity (μS) of the desalination solutions for NH6-NH10.: (L. Naisheng).

The static de-ionized water infusion method was used to desalinate the other five porcelain samples, NH6-NH10, however the desalination time was extended from 1 day to 1 week and the volume of water increased to 4L. The conductivity results are shown in Table 2 and 3 and (Fig. 4).

Results and Discussion

XRF Analyses

Based on the XRF-EDX data in Table 2-1, the major elements in the surface of the recovered porcelain are SiO_2 and Al_2O_3, which is similar to the chemical composition of common undegraded porcelain in China. However there are still some significant differences. For example, the CaO, Fe_2O_3 and SO_3 content is higher in the glaze of the porcelain samples, NH2, NH3, NH10, while the SO_3 content is higher in the body of sample NH2 than other samples. The reason for the increase in these elements may be due to prolonged immersion in seawater.

IC Analyses

Based on the IC results in Table 2-2, there are many soluble ions present in the porcelain samples. The major ions are chloride (Cl^-), sulfate (SO_4^{2-}), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}) and calcium (Ca^{2+}), which are present in the seawater. The total salt content of each sample ranged from 1,000 ppm to 8,000 ppm. Such high concentrations of soluble salts will tend to recrystallise during changes in the environment and cause damage to the glaze and body of the porcelain, so an appropriate method to remove the soluble salts from marine porcelain is extremely important.

Desalination of samples NH1-NH5

Based on the results in Fig. 3, the static de-ionized water infusion method and the heating method to accelerate the desalination process are both very effective and the rates of desalination for both methods are similar. After two days, the conductivity curve of the soak solutions of NH1-NH5 decreased significantly, which means the soluble salts (NaCl, $MgCl_2$, etc.) in the facial layers had been removed. However, after 14 days, the conductivity increased, which indicates that there was still some soluble salts present deeper within the body of the porcelain. After this time the conductivity decreased and plateaued again after approximately 21 days.

These results indicate that for the alternating hot and cold water soaked samples, the conductivity of the soak solutions plateaued after 15 days with the average conductivity being under 1μS/cm. This means the samples had almost reached the desalination end point after this short time period (Naisheng, 2012). The total desalination time for the Nanhai I shipwreck porcelain samples (NH1-NH5) was 25-30 days for the heated desalination method and 50-60 days for the static de-ionized water infusion method.

Desalination of samples NH6-NH10

Fig. 4 shows that after 9 weeks of soaking, the conductivity of the better preserved porcelain samples like NH6, NH7 and NH9 were steady and the average values were under 1μS/cm (Naisheng, 2012), indicating the desalination process had reached its end point. However, for the porcelain samples NH8 and NH10, the conductivity was still around 2μS/cm (Naisheng, 2012), which was slightly higher than the better preserved samples indicating that these samples were more degraded and had therefore not reached their desalination end point after 9 weeks of immersion due to a higher initial salt content. Based on the results of these desalination experiments the static de-ionized water infusion method is an effective and convenient desalination method for the Nanhai I porcelain, especially for the better preserved samples, which easily reached their desalination end point after 63 days.

Conclusions

Based on the results of the XRF-EDX, IC and conductivity tests on the Nanhai I porcelain samples, the conclusions are as follows:

1. Based on the XRF-EDX analysis data, the major elements in the surface of the recovered porcelain are SiO_2 and Al_2O_3, which is similar to the chemical composition of common, undergraded porcelain in China while the concentrations of CaO, Fe_2O_3 and SO_3 are high and maybe due to their prolonged immersion in seawater.

2. IC analysis data shows that the total salt content of each sample ranged from 1,000 ppm to 8,000 ppm, and the main ions present are Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}. Such a high content of soluble-salts within the samples will cause damage to the glaze and body of the porcelain.

3. The results of the desalination experiments indicate that the static de-ionized water infusion method is an effective and convenient desalination method for porcelain recovered from the Nanhai I shipwreck, especially for better preserved porcelain. They easily reached their desalination end point after 63 days.

Acknowledgements

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Biography

Naisheng Li *received his PhD in 2006 from the USTC, Hefei, China. His research field comprises the analysis and conservation of museum objects and underwater cultural relics, such as porcelain, metals, stone, and wooden shipwrecks. Since 2006, he has worked as a conservation and research staff of ancient objects at the Chinese Academy of Cultural Heritage (CACH) in Beijing. He is currently participating in designing the conservation of Nan Hai No.1 Shipwreck.*

Number	Vessel shape	Characteristics	Description
NH1	bowl(mouth rim)	Grey porcelain body, celadon glaze, pattern on the surface.	Body corroded, pulverized and loose.
NH2	fragment	Grey porcelain body, glaze spalling.	Body corroded, very porous; sediment on the porcelain.
NH3	fragment	Grey porcelain body, brown glaze.	The body is weak; the surface of the glaze is bumpy; part of the glaze has peeled off.
NH4	fragment	Grey porcelain body, glaze spalling.	The body is weak; the entire glaze has peeled off.
NH5	fragment	White porcelain body, white glaze	Better extent of preservation; black deposits on the surface.
NH6	dish	White porcelain body, green white cracked glaze; there is a pattern of hemerocallis on the inner part of the porcelain	Pulverization on the body section; fragile, easily broken.
NH7	plate(bottom)	White porcelain body, green white glaze; carving on the inner part of the porcelain; there are five nail marks on the inner bottom of the porcelain.	Brown sediment on the porcelain body; the glaze is yellow and part of it has black deposits.
NH8	bowl(bottom)	Grey porcelain body, green glaze; carving on the inner part of the porcelain.	Better extent of preservation; part of the glaze has white deposits.
NH9	bowl(mouth rim)	Grey body, green glaze; the space between the body and glaze is wider than others.	Glaze corroded; part of the glaze has peeled off; part of the glaze has black and brown deposits
NH10	jar(belly)	Grey body, no glaze on the inner part but brown colored; the surface has brown glaze.	Body is weak and most of the glaze has peeled off.

Table 1: Description of the ten porcelain samples recovered from the Nanhai I.: (L. Naisheng).

Number	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	ZnO
NH1body	2.69	0.67	19.77	68.67	0.10	1.43	3.11	0.29	0.44	0.04	2.74	0.02
NH2body	0.58	0.27	19.24	67.16	0.11	6.12	3.15	0.95	0.07	0.15	2.13	0.02
NH3body	0.19	0.51	23.86	67.01	0.00	0.27	3.12	0.41	0.71	0.11	3.73	0.02
NH4body	0.54	0.71	23.59	68.01	0.00	0.11	2.73	0.26	0.72	0.04	3.19	0.02
NH5body	0.20	0.31	17.49	71.75	0.12	0.18	3.45	5.60	0.06	0.02	0.72	0.01
NH1glaze	0.25	1.64	13.07	60.84	1.39	0.30	2.59	16.14	0.34	1.42	1.94	0.03
NH2glaze	1.15	0.58	12.42	37.11	0.79	22.33	1.96	10.09	0.27	0.58	12.67	0.03
NH3glaze	0.49	3.35	13.14	47.59	2.79	0.40	3.23	19.89	0.51	2.12	6.42	0.06
NH4glaze	0.41	0.61	26.48	61.80	0.08	2.13	3.21	0.25	0.92	0.04	3.95	0.01
NH5glaze	0.65	0.54	15.46	65.92	0.21	0.11	2.88	12.78	0.05	0.10	1.24	0.03
NH6body			22.42	70.63		0.87	2.02	3.10		0.07	0.80	
HH7body			23.11	73.40			2.23	0.45			0.73	
NH8body			24.61	69.48	0.86		1.69	1.23	0.22	0.07	1.77	
NH9body			23.61	71.79			2.04	0.86		0.13	1.52	
NH10body			26.47	69.20			1.19	0.21	0.69		2.20	
NH6glaze			20.64	66.47	2.56	0.29	2.33	6.89		0.06	0.68	
NH7glaze			23.61	63.84	2.60	0.54	2.13	6.04		0.07	0.95	
NH8glaze			19.62	63.55	3.67	0.50	2.12	8.57	0.17	0.29	1.39	0.02
NH9glaze			24.01	68.00			2.22	4.50	0.07	0.48	0.64	0.01
NH10glaze			19.50	52.53	5.24	1.48	1.90	12.07		0.26	6.19	0.04

Table 2-1: The XRF-EDX results for the porcelains recovered from the Nanhai I (wt%).: (L. Naisheng).

Number	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
NH1	493.05	809.13	611.02	100.17	190.32	342.80
NH2	1870.53	631.03	3887.56	400.03	434.95	538.63
NH3	1018.16	237.82	1947.14	260.86	180.59	268.29
NH4	497.17	141.40	862.06	72.98	130.45	98.98
NH5	106.87	73.22	307.99	41.23	95.93	233.94
NH6	493.67	380.95	322.95	52.94	40.25	47.06
NH7	182.28	351.46	487.89	46.14	10.61	113.84
NH8	371.78	382.68	316.03	46.14	37.83	74.63
NH9	136.18	272.00	125.72	46.14	8.30	39.22
NH10	527.85	296.06	644.75	89.50	80.39	119.95

Table 2-2: The IC results for the porcelains recovered from the Nanhai I (µg/g).: (L. Naisheng).

Number	7days	14days	21days	28days	35days	42days	49days	56days	63days
NH6	38.71	6.07	1.83	0.53	0.6	0.18	0.15	1.44	0.7
NH7	15.71	0.35	0.08	0.24	0.34	0.09	0.11	0.33	0.73
NH8	29.98	9.25	8.01	7.43	4.36	2.96	2.79	2.94	2.17
NH9	12.84	2.21	3.16	0.32	3.38	2.03	1.64	0.67	0.43
NH10	251.6	14.13	9.21	4.84	4.85	3.51	3.18	0.8	1.07

Table 2-3: The weekly variation in conductivity of the desalination solutions for NH6-NH10 (µS/cm).: (L. Naisheng).