Research on the removal of calcareous and iron concretions from marine finds

Zhang Zhiguo, Ma Qinglin, Li Naisheng, and Tian Xingling
Department of Conservation Science and Technology for Underwater Cultural Relics
Center for Cultural Relic Restoration and Training
Chinese Academy of Cultural Heritage
No. 2 Gao Yuan Street, Chao Yang District,
Beijing 100029
China
Email: zzgwys@126.com

Liu Wei
University of Science and Technology,
Beijing
China

Abstract

In recent years, several shipwrecks have been found in the South China Sea, such as Huaguang Jiao I and South China Sea I, shipwrecks from the Southern Song Dynasty (12-13c AD) and Nan'ao I, a wreck from the Ming Dynasty (14-17c AD). Many ancient archaeological iron objects were found the site. Usually, calcareous and iron concretions exist on these iron objects and some iron objects are concreted together very tightly. This paper discusses methods to remove calcareous and iron concretions from archaeological iron objects found from the sea and separation methods for the concreted iron objects recovered from the Huaguang Jiao I and South China Sea I shipwrecks.

Key words: Huaguang Jiao, South China Sea I shipwreck, Iron objects; Calcareous; Iron concretions; Removal techniques

Introduction

The most striking feature of iron corrosion in a marine environment is the formation of thick concretions. Concretions form on iron buried beneath the seabed and on that exposed to seawater. In both cases the concretion is formed by the iron corrosion products interacting with material adjacent to the iron. Iron is not a biologically toxic material and any iron immersed in seawater is rapidly colonized by marine organisms. These organisms build up a layer of skeletal material, predominantly calcium carbonate ($CaCO_3$). The subsequent diffusion of iron II ions (Fe^{2+}) and iron III ions (Fe^{3+}) from the underlying corroding iron produces chemical changes in this biological material (North, 1976). In the concretion, Fe^{2+} ions interchange with calcium ions (Ca^{2+}) in the $CaCO_3$, to produce ferrous carbonate or siderite ($FeCO_3$). Some of the $CaCO_3$ is also dissolved by the hydrogen ions (H^+) forming calcium bicarbonate [$Ca(HCO_3)_2$], which causes the pH of the solution to increase. The increasing pH then results in the gradual precipitation of Fe^{2+} and Fe^{3+} as oxides, hydrated oxides and hydroxy chlorides. These fill holes and pores in the concretion and so form an iron cementing matrix to replace the original calcite matrix, which is slowly dissolving. Under the concretion, in areas of low oxygen content, reactions between iron ions and sulphide ions (S^{2-}) ions produced by sulphate reducing bacteria result in the formation of iron (II) sulphides (FeS) and elemental sulphur (S). The end result of these processes is that the inner concretion becomes a replica of the marine growth but with the $CaCO_3$ of the marine organisms virtually entirely replaced by iron corrosion products (North, 1976).

The outer layer of the iron concretions is approximately the same composition as the marine growth on inert materials. The major differences are the presence of up to 2% iron and small, but significant amounts of inorganic $CaCO_3$. When iron is continuously buried beneath the seabed, negligible marine growth occurs but a hard concretion can still be formed provided the seabed material contains $CaCO_3$. The mechanism here appears to be basically the same as for exposed iron. As the iron-rich acidic solution diffuses into the surrounding seabed material it dissolves some $CaCO_3$ and precipitate iron compounds which act as a binding cement. Further out from the object the previously dissolved calcium reprecipitates, due to increasing pH, and forms a second cementing layer. As a result any material in the seabed next to the corroding iron is incorporated into the concretion. Magnetite (Fe_3O_4) is the main iron oxide component of buried concretions compared with iron oxy hydroxides (FeOOH) and haematite (Fe_2O_3) in exposed concretions (North, 1987a).

The concretions from the *Batavia* shipwreck site in Australia mainly contained FeOOH, Fe_3O_4, $FeCO_3$ and iron hydroxy chlorides (FeOCl), minor constituents were $CaCO_3$, quartz (SiO_2), FeS and S and sometimes contained traces of sodium chloride (NaCl) and gypsum ($CaSO_4.2H_2O$) (North, 1976). North (1982) compared the chemical compositions of concretion and iron corrosion products from the *Day Dawn* shipwreck site in Australia, the concretions consisted of 46.1% iron (Fe), 0.34% sodium (Na), 7.9% calcium (Ca), 0.33% magnesium (Mg), 2.2% SiO_2 and less than 0.05% chlorine (Cl), but the iron corrosion products consisted of 60.8% Fe, 0.06% Na, 0.11% Ca, 0.03% Mg and 6.1% Cl (North, 1982). Concretions found within marine sediment, where oxygen is relatively scarce, contain higher proportions of lepidocrocite (γ-FeOOH), Fe_3O_4, and the magnetic sulphide, pyrrhotite ($Fe_{1-x}S$). Other compounds, which are unstable under atmospheric conditions, and thus difficult to identify, may also by present (Cronyn, 1990). The main method of concretion removal is by mechanical methods, such as toothpick, dental drill, riveting gun, hammer and sand-blasting machine (Hamilton, 1999; Mardikian and David, 1996; North 1987b; Rees-Jones, 1972). Chemical methods, such as 20% phosphoric acid (Rees-Jones, 1972) and hot soda baths (Pearson, 1972), have been used, especially for seriously corroded fragile iron, but concreted iron objects cannot be soaked for a long time. Liquid nitrogen (MacLeod, 1987) and electrolytic methods (Montlucon, 1986) can also be used for concretion removal. The liquid nitrogen method is effective in removing thick calcium carbonate layers on iron surfaces. Hydrogen produced by the electrolytic method may cause damage to the surfaces of ancient iron objects.

The concretions on some marine iron recovered from three shipwrecks excavated from the South China Sea, *HuaguangJiao I* and *South China Sea I*, wrecks from the Southern Song Dynasty (12-13c AD) and *Nan'ao I,* a wreck from the Ming Dynasty (14-17c AD), were analysed using multiple scientific techniques to determine the composition and structure of the concretions. The concretions from the three wrecks are composed primarily of two different types; calcareous/iron concretions or coral and siliceous concretions. The different types of concretion from the three wrecks were comparatively analysed. The results indicated that the concretions from *South China Sea I* contain calcareous and siliceous concretions, mainly SiO_2, mixed calcareous concretions, FeS_2, and $FeCO_3$. And concretions from *HuaguangJiao I* were analogous to those from *Nan'ao I* except the composition of the iron concretions from the former consisted primarily of Fe_3O_4, goethite (α-FeOOH), lepidocrocite (γ-FeOOH), Fe_2O_3 and akaganeite (β-FeOOH), while FeS, $FeCO_3$ and β-FeOOH were the main minerals present in the *Nan'ao I* iron concretions (Liu et al., 2011). This paper discusses methods to remove calcareous and iron concretions from marine archaeological ancient iron objects and tests some separation methods for the concreted iron objects from the *HuaguangJiao I* and *South China Sea I* shipwrecks.

Results and Discussion

Removal of the Calcareous Concretions by Chemical Methods

Fig. 1 Iron object (HTQ-9) from the HuaguangJiao I shipwreck. (Z. G. Zhang).

Figure 1 shows the white calcareous concretions on the iron object, HTQ-9 from the *HuaguangJiao I* shipwreck. The calcareous concretions are usually composed of two layers, an outer and inner layer. Two samples of the different layers were collected using a scalpel. The outer white surface layer consisted of calcite ($Mg_{0.1}Ca_{0.9}CO_3$) and aragonite ($CaCO_3$) and the inner white layer consisted of kutnahorite ($Ca_{1.11}Mn_{0.89}(CO_3)_2$ and $CaCO_3$. Figures 2a and 2b show the XRD spectrums of the outer and inner layer samples. The calcareous concretions of two layers are both very hard, and the inner layer is harder than outer one. About 0.4g of the white calcareous concretion, removed from the outer and inner layer of iron object HTQ-9, was soaked in a 10% EDTA disodium salt solution (EDTA-2Na), pH value was about 10. Figure 3 shows the transformation process of the concretion sample. The sample had completely dissolved after 102 hours. This experiment demonstrates that 10% EDTA-2Na can remove these types of white calcareous concretions present on this marine iron object.

Removal of the Iron Concretions by Chemical Methods

The iron object of HTQ-17 from the *HuaguangJiao I* shipwreck was sectioned into five sub-samples. The size of each sample was about 3.0 square centimeters. The red brown iron concretion on their surface was analysed by XRD. Figure 2c shows the XRD spectrum. The analysis result indicated the concretion mainly consisted of β-FeOOH, γ-FeOOH, Fe_3O_4 and α-FeOOH. Five solutions; 5% oxalic acid, 10% oxalic acid, 9.35% aminoacetic acid, 9.35% aminoacetic acid sodium salt and 9.35% mercaptoacetic acid sodium salt, were tested to dissolve the red brown iron concretions on five samples of

HTQ-17. Figure 4 shows the transformation of the red brown iron concretions of HTQ-17 in 9.35% mercaptoacetic acid sodium salt. The results of the experiment demonstrated that the dissolution rate of the red brown iron concretions in each solution in decreasing order was: 9.35% mercaptoacetic acid sodium salt, 9.35% aminoacetic acid, 9.35% aminoacetic acid sodium salt, 10% oxalic acid, 5% oxalic acid. So the 9.35% mercaptoacetic sodium salt was the best solution to dissolve the iron concretions.

Removal of the Iron Concretions by Mechanical Methods

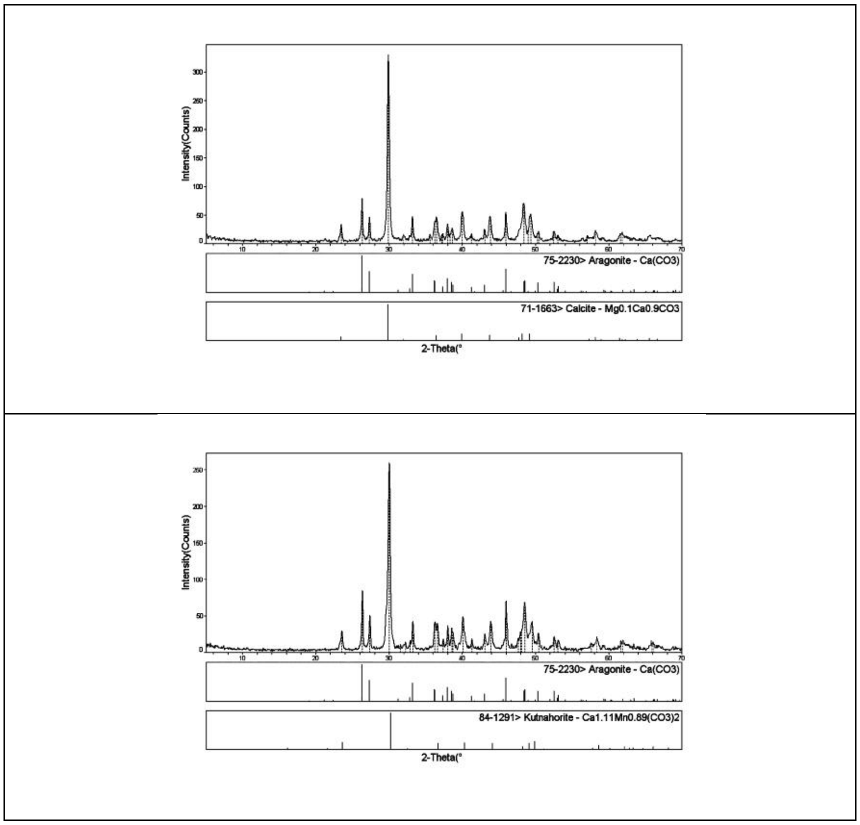
Laser blasting, sandblasting and ultrasonic cleaning methods are effective techniques to remove concretions from marine iron objects (Hamilton, 1999). However, the laser method has the disadvantage that the power is difficult to control; it is an expensive technique and is not suitable for large areas and/or thick concretion layers. Sandblasting is appropriate for the more fragile iron objects with thin concretion layers. Ultrasonic cleaning, such as an ultrasonic dental tool, is useful for deconcreting small areas covered in thin concretion layers, which are not particularly hard and the power is easily controlled. Mechanical and chemical methods are commonly used in combination to remove concretions from marine iron objects. Figure 5a shows a concreted iron nail recovered from the *South China Sea I* shipwreck. The concretion was removed using a combination of mechanical and chemical techniques, i.e. a solution of EDTA-2Na in conjunction with a chisel and scalpel were used to remove the concretion from this object. Figure 5b shows the iron nail after concretion removal.

Separation of a Group of Concreted Iron Objects

Figure 6a shows a group of four concreted iron objects, HTQ-2 recovered from the *HuaguangJiao I* shipwreck. Some mechanical tools, such as an electric drill, an engraver, a chisel and a small hammer were used to mechanically separate the iron objects. Special care was taken during the separation process to avoid any fracture or breakage. When the electric drill was used for separation, the appropriate diameter drill bit was chosen and the power should be controlled according to the extent of corrosion and the distance between the concreted iron objects. Figure 6b shows the four iron objects after separation.

Conclusion

This paper presented some experimental results on a variety of removal methods for calcareous and iron concretions from marine archaeological ancient iron objects. Based on the analytical data, 10% EDTA-2Na can remove the white calcareous concretions on marine iron objects and 9.35% mercaptoacetic acid sodium salt solution can dissolve the red brown iron concretions successfully. Commonly combinations of mechanical and chemical techniques can remove block concretions on marine iron objects and separate groups of concreted iron objects. Mechanical techniques are still the most common and reliable method for concretion removal.



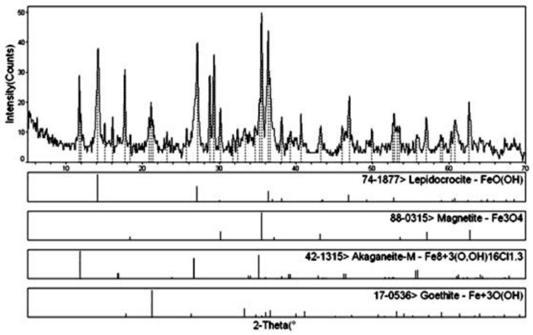


Fig. 2 XRD spectrum of HTQ-9 (a = outer layer; b = inner layer) and HTQ-17 (c).
(Z. G. Zhang)

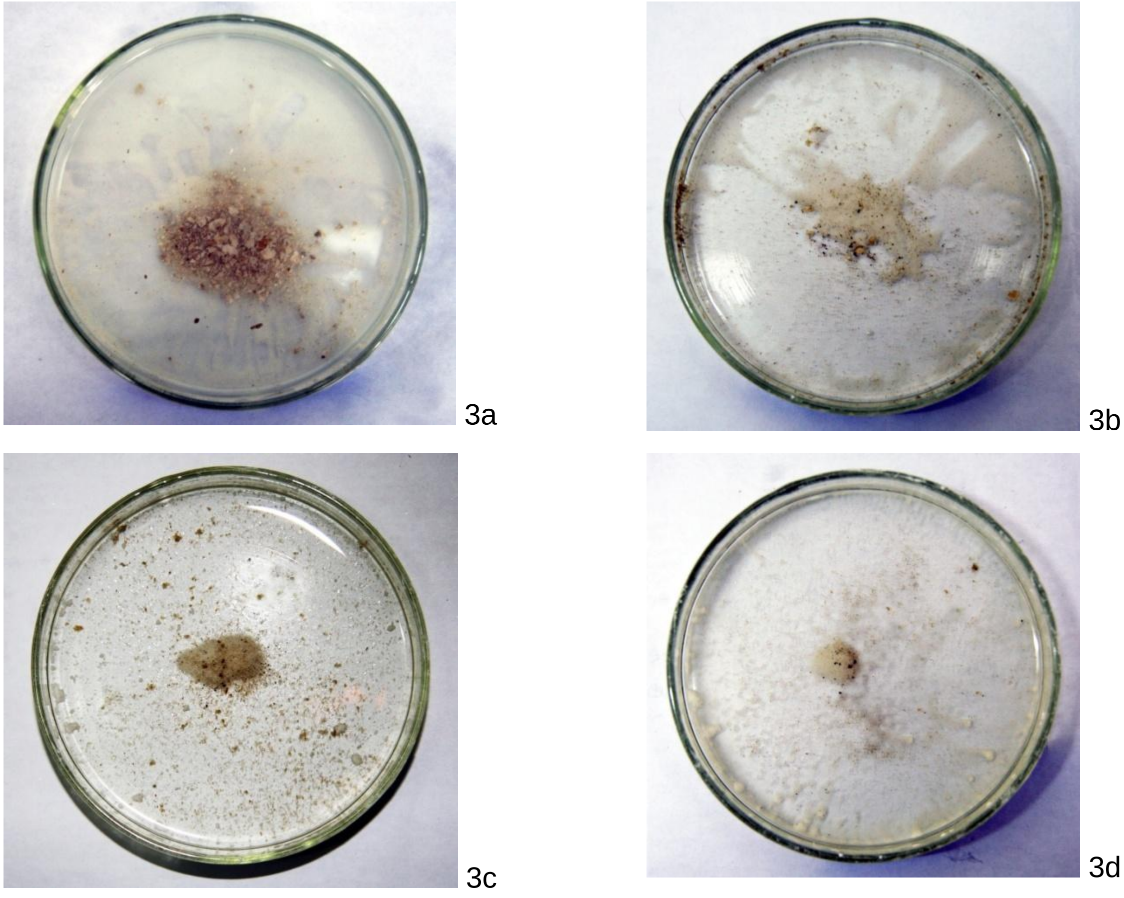


Fig. 3 Transformation of calcareous concretions from HTQ-9 in 10% EDTA disodium salt after (a) 0 hours, (b) 6.5 hours, (c) 54 hours, (d) 102 hours. (Z. G. Zhang)

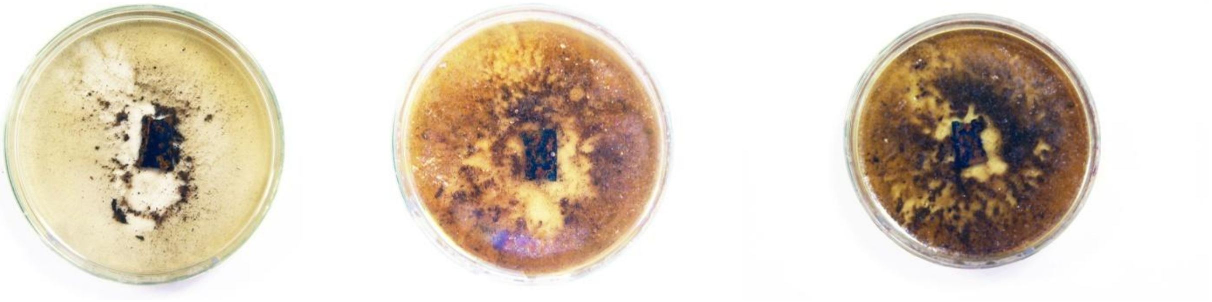


Fig. 4 Transformation of the red brown iron concretions from HTQ-17 in 9.35% mercaptoacetic acid sodium salt after (a) 24 hours, (b) 72 hours, (c) 144 hours. (Z. G. Zhang)

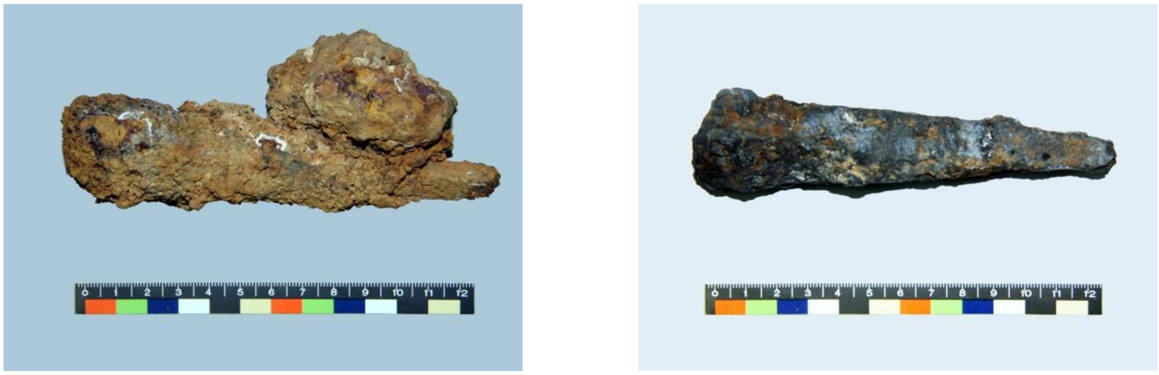


Fig. 5 Iron nail from the South China Sea I shipwreck. (a) Before deconcretion, (b) After concretion removal. (Z. G. Zhang)

Fig. 6 Concreted group of iron objects, HTQ-2 from the HuaguangJiao I shipwreck (a) Pre-separation, (b) After separation. (Z. G. Zhang)

Acknowledgements

We would like to thank Mr. Qiu Gang, Director of Hainan Museum, who supplied the marine iron samples. We would also like to thank Prof. Zhan Changfa and Dr. Shen Dawa for their assistance with the analysis and research. This research project was financially supported by the Chinese Academy of Cultural Heritage (CACH).

References

Cronyn, J. M., 1990. *The Elements of Archaeological Conservation*. Routledge Press, Britain, 181.

Hamilton, D. L., 1999. *Methods of Conserving Archaeological Material from Underwater Sites*. Nautical Archaeology Program. Department of Anthropology. Texas A&M University. College Station, Texas, 54-55.

Liu, W., Wang, J. L., and Zhang, Z. G., 2011. Scientific analysis of the concretion on ancient marine iron recovered from three shipwrecks in South China Sea. *Journal of National Museum of China*, Vol. 2: 145-156.

Mardikian, P., and David, R., 1996. Conservation of a French pistol from the wreck of *Le Cygne* (1808). *Studies in Conservation,* Vol. 41: 161-169.

MacLeod, I. D., 1987. Conservation of corroded iron artefacts - new methods for on-site preservation and cryogenic deconcreting. *International Journal of Nautical Archaeology and Underwater Exploration*, *Vol.* 16 (1): 49-56.

Montlucon, J., 1986. Electricity: A new implement in archaeology. In J. W. Foster and O. S. Sheli (Eds.), *17th Conference on Underwater Archaeology*. *Sacramento, California,* January 8-12, 1986, Facsimile Reprint by Coyote Press: 75-78.

North, N. A., 1987a. Corrosion of metals. In C. Pearson (Eds.), *Conservation of Marine Archaeological Objects*, London, Butterworths: 77-78.

North, N. A., 1987b. Conservation of Metals. In C. Pearson (Eds.), *Conservation of Marine Archaeological Objects*, Butterworths, London, 209-211, 223-227.

North, N. A., 1982. Corrosion products on marine iron. *Studies in Conservation*, Vol. 27: 75-83.

North, N. A., 1976. Formation of coral concretions on marine iron. *International Journal of Nautical Archaeology and Underwater Exploration*, Vol. 5 (3): 253-258.

Pearson, C., 1972. The preservation of iron cannon after 200 years under the sea. Studies in Conservation, Vol. 17: 102.

Rees-Jones, S. G., 1972. Some aspects of conservation of iron objects from the sea. *Studies in Conservation*, Vol. 17: 39-43.

Biography

Zhiguo Zhang *received his BSc (2001) and MSc (2004) in Chemistry from Shandong University and Tsinghua University, respectively and attained a PhD (2011) in history of science and technology from the University of Science and Technology, Beijing, China. His research field comprises the analysis and conservation of museum objects and the protection of marine cultural relics, such as ancient Chinese pigments, metals, stone, and wooden shipwrecks. Since 2004, he has worked on the conservation and research of ancient objects at the Chinese Academy of Cultural Heritage (CACH) in Beijing.*