Conservation Management of Iron Steamships - The SS Xantho (1872)

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SUMMARY

The steamship Xantho has provided the ideal testing ground for the biological and electrochemical analysis of a complex wreck site consisting of the lead sulphide ore galena, the cast and wrought iron engine and all the associated copper alloys pertinent to the operation of such a vessel. This paper reports on the use of sacrificial anodes to arrest corrosion and begin conservation in-situ and on the stabilisation of the historic steam engine built by Penn of Greenwich in 1861.

Metallurgical analysis of the iron and steel combined with electro microprobe studies of concreted metal reveals not only the work history of the vessel but also the changing micro-environment as the wreck is alternatively buried and exposed.

INTRODUCTION

The wrecking of Western Australia's first iron steamship at Port Gregory in 1872 has provided latterday maritime archaeologists and conservators with a model system for the development of management strategies. (McCarthy 1988, MacLeod 1986). The SS Xantho was built in 1848 and converted from a paddle steamer to a screw driven vessel in 1871 with an 1861 engine by Penn & Son of Greenwich. Although salvaged at the time, significant portions of the original structure remained when the site was discovered in 1979.

The overall impression of an iron shipwreck site is often dominated by the remains of the boiler and the frames that once gave the vessel its form. Since corroding iron and steel in seawater is not biologically toxic it rapidly becomes encapsulated by encrusting organisms such as coralline algae and bryozoa (North 1982). This encapsulation begins the process of separating the anodic and cathodic sites of the corrosion cell, with oxygen reduction generally occurring on the outer surface and oxidation of the metal occurring underneath the marine growth (MacLeod 1989). The corrosion process results in the inward diffusion of chloride ions from the sea through the marine growth to the corroding metal and the outward diffusion of the metal ions towards the seaward surface.

Since the concretion acts as a semi-permeable membrane, a hundred years of corrosion results in a substantially different micro-environment being established for the metal itself compared with the surrounding sea. For example, the chloride concentration can be increased by a factor of 3 above the mean seawater levels and the pH can fall from the normal value of 8.2 to as low as 4.2 (MacLeod 1989-2). It is the job of the conservator to ensure that the iron artefacts are safely transported from the seabed to a treatment facility. Removal of the concretion without immersion into alkaline media results in accelerated corrosion of iron in a chloride-rich acidic microenvironment, and the loss of much of the archaeological values (MacLeod 1981).

1. ANALYSIS OF THE SS XANTHO SITE

1.1 Marine Biology

A most significant aspect of the site was that it was essentially untouched and as such presented an excellent opportunity to examine the physical, chemical and biological condition of an iron shipwreck in its undisturbed condition. Such studies have not only intrinsic merit in terms of pure scientific research but they are also invaluable when applied to the excavation and conservation of historic shipwrecks.

Initial inspection of the Xantho site showed up significant differences in the ecosystem compared with a nearby reef which was dominated by eel-grass communities with a large fauna of herbivores feeding on the organisms that lived in the grass. The shipwreck site was a tunicate dominated community with sedentary filter feeders being the major colonising organisms with upright and encrusting sponges and a few encrusting bryozoa. Small chlorophytans (algae) were found in the light rich areas (water depth 2.9-3.3m) while large phacophylans were abundant in water deeper than 3.3 metres. The ships boiler provided a very good area for studying the effects of the current on the marine growth since its long axis was essentially parallel with direction of the strong current which ran at between 3 and 5 knots (1.5-2.6m/sec). The boiler was approximately 3.2m long, 2.8m wide and 2.6m high (see fig. 1). The detailed observations on the biology of this structure has been previously reported (MacLeod 1986). The strong current carried a large amount of weed and sea-borne grit which gave a turbidity of 2.5-3.0 m at best but often it was less than one metre. There appeared to be a marked change in the colonisation of the boiler at a depth of 4.2±0.1m. The chemical environment was typical of the coastal waters of Western Australia with a salinity of 37,53 parts per thousand and the pH of the seawater was 8.1 with a water temperature of 23°C. The Xantho cargo had consisted of the lead ore galena (PbS) and the bulk of it remained on the site. Upstream of the galena, the seawater had the normally expected concentration of lead viz. <0.01ppb. while immediately downstream of the

principal ore mound the lead level was 115ppb. (Jack 1985) i.e. a factor of more than 11,500 times higher. The high lead levels in the seawater were also reflected in the higher amounts found in the concretions, the engine concretion contained 140ppm lead compared with 61ppm in material recovered from the Vergulde Draeck (1656). The latter vessel had many lead fittings such as scuppers and associated pipes which would have been the major source of lead.

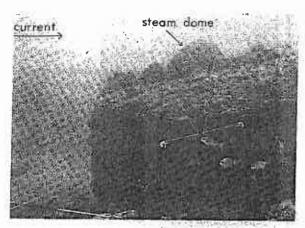


Figure 1 The Xantho boiler viewed from the port side during the predisturbance survey. The grid scale is 1.0 metres. Photo by Pat Baker.

Analysis of the corrosion layers around a copper wire in a water cooling device from the engine room showed that there were a number of corrosion layers. When the logarithm of the spacings between the layers was plotted against the number of growth rings the linear relationships showed that the corrosion phenomena on that site can be described in terms of the liesegang phenomena, i.e. of periodic precipitation (MacLeod 1986-2). The precipitation of the copper sulphides as the corrosion products occurs with the change of the microenvironment from being aerobic, when the object was exposed to the strongly flowing seawater, to anaerobic when two metres of sand were deposited on the site. The rapidly changing nature of the seabed was noted in 1864 when the Zephyr found a discrepancy of 2.1m in the charted water depth and grounded at Port Gregory (Henderson 1988). In the space of the last 110 years approximately 16 bands were found in the corrosion product layers on the artefact and it seems not unlikely that the site has been buried and exposed at least that number of times. The "newness" of the biological environment on the wreck site compared with the surrounding reef is most probably due to the fact that the whole site is periodically buried under several metres of sand. It may be that such burials are due to the scouring of the upstream beaches during heavy winter storms.

1.2 Electrochemical Environment

During a corrosion survey we found that the engine was functioning as a discrete electrochemical entity and that it was electrically isolated from the remains of the hull and the stem section as well as from the propeller and drive shaft. The indications from our measurements were that the engine was in a state of advanced decay and since archaeological drawings

confirmed that it was the world's only surviving example of the first mass produced high pressure marine steam engine. it was decided that something had to be done to stop this piece of industrial heritage falling apart. As a result of our survey, sacrificial anodes were placed on the engine and measurements of the corrosion potential shortly after the anodes were attached showed that we were getting quite reasonable protection with a drop in corrosion potential of over 120mV (MacLeod 1986). However, the sea has many surprises, for when we came back eight months later only the top of the boiler was exposed. What had happened was that the seabed had risen by more than 2m in a space of only eight months. The aluminium anodes placed on the engine were chosen since they function very well in oxygenated water, however, we found that they didn't function too well buried under 2m of clayey sand! Subsequent placement of anodes has seen the use of zinc metal which continues to function effectively even when buried in the marine sediment (Shrier 1976).

During the corrosion potential (E__) survey it was noted that many of the concretions evolved gas when penetrated by the drill. The E_{con} values show that the iron is often in strongly reducing conditions with Eh values at -0.310 volts at pH 4.8, i.e. just below the hydrogen evolution potential for the same pH. Hydrogen has been identified as a major component of the gases released when concretions are penetrated for the first time in centuries (MacLeod 1988). Amongst the other gases were carbon dioxide (from acid dissolution of calcite and aragonite as a result of hydrolysis reactions) and methane. Since methanogenic bacteria are often active in strongly reducing conditions similar to those observed under some concretions, it was essential to determine if the CH, was of inorganic or biological origin. Since bacteria effectively fractionate carbon isotopes in favour of 12C, the isotope shift $(\delta^{13}C)$ has values -55 to-75ppt (relative to the standard limestone, PDB) for bacterially produced methane (Hunt 1979). The observed isotope shift was -4.7ppt which showed that the methane was inorganically derived via reactions such

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
 (1)

Inspection of the carbon Pourbaix diagram shows that methane is the thermodynamically stable form of carbon under the lower portion of the range of Eh and pH (Pourbaix 1974).

2. SACRIFICIAL ANODES

Our E_{cor} measurements on the engine before, during and after the use of sacrificial anodes showed that this simple exercise effectively halted further deterioration of the historic engine. Since the recovery of the stern section was to take place some time in the future it was decided to treat the wrought iron and steel section in-situ.

Two 28kg zinc anodes were attached through six 'G' clamps to various parts of the stern section. The stern section had previously been separated from the rest of the vessel by

cutting with a thermal lance (Kimpton 1988). By machining the threaded shaft on the clamps to a fine point, it is possible to get good electrical contact with the underlying metal by tightening the thread using the built-in handle. Under such compression the shaft penetrated the 4cm thick concretion to provide a good electrical connection which was confirmed by in-situ resistance measurements. Insulated copper cables were brazed onto the 'G' clamps and the central steel core of the zinc anodes to provide electrical contact. The cost of two 28kg zinc anodes, six 'G' clamps and associated cable and composition as \$250, which is very small when placed against the values of the wreck material. With the outward diffusion of collorder ions occurring during cathodic protection, it may be possible to perform major parts of a conservation freatment of mathematical residues object is raised (Fig.2)



Figure 2 Attachment of sacrificial anodes to the propeller with a G clamp. Photo Jon Carpenter.

Measurements of the surface pH of the stern section after 20 months of treatment showed a fall in acidity, with the pH being 6.6 compared with an original value of 4.8 which represents more than a sixty-fold reduction in acidity. This confirms the predictions made in the laboratory as to the effectiveness of this approach.

Recent work on a concreted iron cannon from the Batavia (1629) has shown that chloride ions diffuse out from the dense concretion under the influence of the electrical current flowing from the sacrificial anode and at rates up to 8.7g.m². hr ¹⁸ (MacLeod 1988). A formal representation of one of the many processes occurring during the cathodic protection of the iron sections can be summarised by the equation

2FeO.OH + FeCl, + 2e- \rightarrow Fe,O, + H, +2Cl- (2)

namely, a mixture of iron (II) and iron (III) corrosion products are changed from the reactive and inherently acidic forms to the stable, black corrosion product magnetite (Fe,O2). In the same process the chloride ions diffuse through the concretion back into the surrounding seawater and the acidity of the solution under the concretion is reduced. The reduction in acidity shifts the iron metal towards a more stable situation. Since the acid from metal ion hydrolysis had dissolved calcium carbonate, the reduction in acidity will tend to promote redeposition of calcium/magnesium carbonates magnesium calcites) and the deposition of the iron carbonate aderate (FeGO;). Such a redeposition would harden the concretion and combined with the production of more magnetite, it would act as a "cement" to bind together the original surface material which normally falls away from the correded metal. The filamentous nature of the slag inclusions (SiO: 2FeO) in wrought iron may act as a reinforcing matrix for the redeposited minerals and result in more of the original structure being preserved for the purposes of display and research.

3. CORROSION AND WATER MOVEMENT

During the initial survey it was noted that the apparent extent of corrosion varied quite markedly. The windlass contained no solid metal and the E values for the engine, boiler, etc. all seemed to be similar while the frames near the stern reflected lower corrosion rates. Subsequent work on the HMS Sirius site led to the development of a new corrosion model that showed systematic differences in E between wrought and cast fron of approximately 70mV for the same water depth (MacLeod 1989). The model also demonstrated that the corresion rate is very dependent on water depth and the flux of dissolved oxygen. When the Xantho on-site data is reviewed in the light of the new model it makes much more sense. The worst affected items such as the windlass were at a shallower depth and exposed to localised eddying of current, while the engine was sheltered behind the boiler and was at a greater water depth. The corrosion potentials for the wrought iron objects such as the boiler and frames can be compared with cast iron if "corrected" by 70mV for the enobling effect of the carbon. Thus the E_ of the boiler (see Table 1) becomes "-0.200 volts" which puts it on a par with the deck winch in terms of the corrosion micro-environment. It also is consistent with E shifting more positively by 18.9±1.5 mV for every metre less in the depth of water. On the basis of this understanding we can confidently predict that the best option for the boiler is to leave it on-site since there will be very little solid metal remaining in the structure.

Armed with a knowledge of water depth and site profiles and the way in which water moves over a wreck, it is possible to interpret the corrosion potentials on iron shipwrecks and to develop appropriate management strategies. The temperature effects on corrosion potentials have not been directly determined, but repeated measurements of the Xantho boiler at Port Gregory (MacLeod 1988) over a period of four years gave an E_{corr} of -0.274 ± 0.003 volts with the temperature at

4 metres depth ranging from 18.5-25.0°C. The small variation in $E_{\rm corr}$ values indicates that after more than 100 years immersion the objects are not as sensitive to temperature effects as objects at 30 days exposure (LaQue 1975).

TABLE I

Effects of composition and site conditions on corrosion potentials*

Object Ecorr		Cast Iron		Wrought Iron	Site Details	
Windlass	-0.103	Y.		· N	ne solid metal, exposed to full current flow	
Water Heater	-0.163	Y	សង្គាន	N-	attached to copper costs	
Deck Winch	-0.216	Y	5 ;	N5-	relatively exposed condition	
Engine	-0,268	Y	4.5	N-	shaltered beland boiler	
Propellor shaft	-0,268	Y.	4.5	Ň	bedded down in hall	
Boiler	-0.270	N.	2.5-3.5	Y	bears full brunt of current	
Frames and plates at stem	-0.280	N	4	Y	half buried in earld, but upper section not protected.	

Potentials were measured with a platinum electrode using a Ag/AgC1 seawater reference which was calibrated using the voltage of the platinum electrode in a pH 4.0 solution saturated with quinhydrone.

4. METALLURGY OF THE XANTHO ENGINE

During the corrosion survey on the concreted engine it was noted that the counterbalances on the crankshaft contained lead - the drill bit had cut through the concretion to reveal a soft white metal. After excavation we found that the measurement point was where the lead came to the surface at the filling point of the hollow cast iron sections. Not unexpectedly the non-ferrous fittings on the engine showed little corrosion owing to the fact that they had been cathodically protected by the bulk of the cast and wrought iron of the engine. However, it was noted on the large copper steam exhaust pipe that the surface had been attacked, leaving the distinctive pattern of the serpulid polychaete worm casts etched into the metal. These worms appear to be unaffected by the toxicity of the surface oxides and the secure attachment over sections of the pipe leads to the development of differential aeration cells (see fig.3).

Since the Xantho sank in November it would have been the optimum time for colonisation by marine organisms. All the copper, brass and bronze fittings were covered with a thin, adherent white calcareous concretion typical of a cathodically protected artefact recovered from a wreck site (MacLeod 1982). Mechanical removal of the concretion showed a dark grey-blue patina on the surface of the artefact and on the inside face of the concretion. The colour is due principally to copper sulphides which form under anaerobic conditions that arose when the engine was periodically buried. The copper pipes were generally joined with a brazed overlapping seam.

As the concretion came away from the surface of a bronze tallow pot it showed up the metallographic structure of the superbly cast fitting. Analysis of the grey-black material under the CSIRO (Floreat) SEM showed up sulphur, zinc, tin, copper and a trace of lead. The "texture" of the corrosion products showed that the bronze object had a metallographic

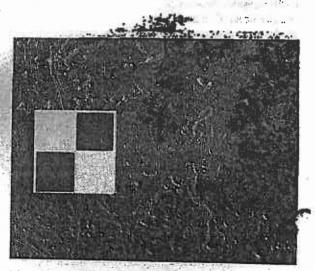


Figure 3 Corrosion of copper steam pipe caused by serpulid polychaete worms. Scale is 2cm. Photo Jon Carpenter.

structure consisting of the "Chinese script phase" with average diameter of the characters being approximately 260µm (see Fig 4). The sulphur came from anaerobic bacteria and the zinc levels were typical of a zinc tin bronze.

The material was further examined by X-ray diffraction and the major phase was the tin sulphide Sn₂S₃ and a minor component of the polysulphide, Cu₂S. The formally mixed oxidation state of the tinsulphide, i.e. a mixture of tin (IV) and tin (II) indicates that the site conditions may have been not very strongly oxidising; this supposition is supported by the presence of the non-stoichiometric sulphide Cu₂S.

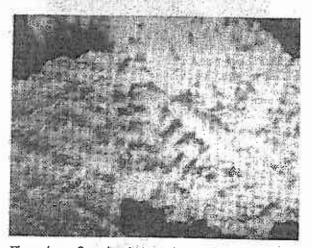


Figure 4 Scanning electron micrograph of tin and copper corrosion products from a bronze tallow pot.Full width 2500µm.

Previous research on the Rapid site has shown that under anaerobic conditions there will be preferential corrosion of base metals according to the thermodynamic stability of the parent sulphides. It is therefore not unexpected that the burial of these engine fittings lead to selective corrosion (etching) of the tin and zinc rich phases of the bronzes and brasses. Since the fittings were located on the upper part of the valve chests they would have been buried to a smaller extent than other fittings closer to the bottom of the engine and so the effects of the burial would not be as great.

A riveted joint from the 1871 rebuild of the stern of the iron steamship Xantho was sectioned and analysed to determine if corrosion problems had been the primary cause of the wreck (see Table 2). It had been reported (McCarthy 1988) that the 'plates had sprung' in a storm immediately prior to the vessel sinking at Port Gregory in 1872. The sectioned piece of metal included a rivet body and head that had bonded three sheets of 6-7mm thickness which had been interleaved with linen prior to joining (see Fig. 5). The chemical analyses of the sheets are reported in Table 2 and are typical of wrought iron of that beriod. Metallographic examination of the junction shows "flow lines" in the head and body of the rivet which result from segregation of the different metal components; the various inclusions become elongated into long fibres as a result of forging (Johnson 1944). The microstructure consists of ferritic angular grains of different size - where the inclusions are most numerous the grains are smaller because the elongated inclusion phase stopped their growth. Although there are no traces of cold deformation in the grains, the microhardness measurements show major differences in their average values. In a transverse section, the body of the rivet had a mean value of 277±26 HV which is the same as in the head except for areas adjacent to the "flow lines" where values ranged from 323 to 442 HV. The mean microhardness of the plates was the same as in the body of the rivet. At the junction of the rivet and the top sheet the deformed elongated inclusions resulted from the joining process and from the production of the sheet.

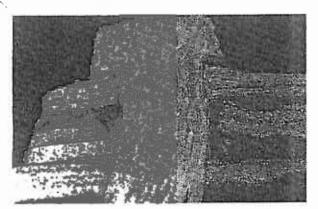


Figure 5 Cross section of rivet and metal plates from the stern section; head of rivet 2.35cm.

All of the sheets and rivet are characterised by a massive number of metallic and non-metallic inclusions including two phase slag particles of FeO in a 2FcO.SiO₂ matrix. Many of the inclusions are fragmented as a result of hammering. A feature of the microstructure of the sheets is that impurities in the metal have been elongated in two directions - longitudinal and in cross-section. Since the degree of impurity elongation is greater in the longitudinal direction then it can be assumed that it was the main direction of rolling with the first stage of production including rolling in both directions. Examination of the section showed that significant corrosion had occurred in the crevice-like spaces in between the sheets. It is impossible to determine how much of the overall corrosion had taken place prior to the vessel's demise. However, given that preferential corrosion occurred along the lines of extensive working adjacent to areas of greater hardness, it is not inconsistent to blame extensive interseam and stress corrosion for contributing to the demise of the vessel.

The composition of the forward valve chest is similar to that for a modern heavy-duty Class 50 cast iron (McGuire 1975) except that the manganese and phosphorous levels are very high (see Table 2). The high phosphorus content would made the parts hard wearing, but might make the metal more brittle. Inspection of the deconcreted engine showed a much more pitted and rough surface on the port and starboard pumps. The pumps were directly connected to the crankshaft by a "Scotch Yoke" type arrangement that did not allow them to be disconnected. Samples of the metal were obtained and a metallographic analysis of the inspection plate was undertaken to see what the underlying causes were for the different materials performance of the pumps compared with the rest of the engine. Although the carbon equivalents of the inspection plate and valve chest were similar (see Table II) the higher silicon content and lower manganese levels tend to promote a random distribution of graphite as superimposed and interconnected flakes in the ferritic matrix rather than having more of the carbon combined with iron to form more pearlite. The mode of corrosion is clearly along the grain boundaries around the "inert" graphite flakes. There was also significant porosity associated with the casting. These factors plus the natural orientation of the long axis of grains perpendicular to the surface of the casting mould (Rhead 1945) would have contributed to the ready ingress of the chloride ions and thus the greater extent of corrosion. A fine white deposit on the inside of the inspection plate was examined with an SEM and shown to be crystals of aragonite (CaCO,) which is consistent with "soft steam" having powered the pumps (see fig. 6).

CONCLUSION

The recovery of the engine from the historic steamship Xantho (1872) has provided conservators and maritime archaeologists with a real challenge. In the last seven years 48.1 kg of chloride ions have been extracted from the engine (1.00 wt%) and 2544 kg of marine concretion and corrosion products have been removed. The Xantho project has lead to a new understanding of the interaction of iron shipwrecks with their microenvironment and has seen the beginning of in-situ conservation processes. As details of the engine construction are revealed one can only gain increased respect for the Victorian engineers and tradesmen. Much more remains to be done in the area of interpretation of the complex biological and corrosion phenomena but the benchmark of this type of heritage resource has been established.



Figure 6 Scanning electron micrograph of aragonite crystals recovered from inside the starboard pump. Full width 260um.

Table 2

Composition of iron alloys on the SS Xantho-1

	Inspection Plate, starboard pump	Starboard pump	Forward. valve chest	Stern Plating	Rivet
CE*	3.42	4.06	3.59	0.395	0.24
С	2.42	2.95	2.65	0.165	0.030
S	0.07	0.06	0.13	0.03	0.01
Mn	0.709	0.81	1.05	0.022	0.045
P	0.58	0.92	1.10	0.33	0.25
Si	2.43	2.42	1.73	0.36	0.38
Ni	0.016	0.017	0.015	0.053	0.035
Ċu	0:013	0.011	0.045.	0.022	0.048
CI	<0.01	0.0175	0.0175	0.02	0.02

^{&#}x27;Samples were obtained by drilling solid metal sections.

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^{*} CE is the carbon equivalent which is defined as wt% $[C+^{1}/_{3}(P+Si)]$.

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