

**THE EXCAVATION, ANALYSIS AND CONSERVATION OF SHIPWRECK SITES**

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**SUMMARY**

The wreck site of the iron steam-ship *Xantho* has provided a model for how an underwater archaeological site can be managed. Pre-disturbance surveys of the marine biology and the electrochemical and physical environment of the site established reference criteria for monitoring changes in the site conditions. Installation of a sacrificial anode system prevented further deterioration of the historically significant engine whilst conservation facilities were being constructed. Measurements made after excavation of the engine established that the removal of this massive structure did not significantly change the microenvironment of the remaining parts of the vessel.

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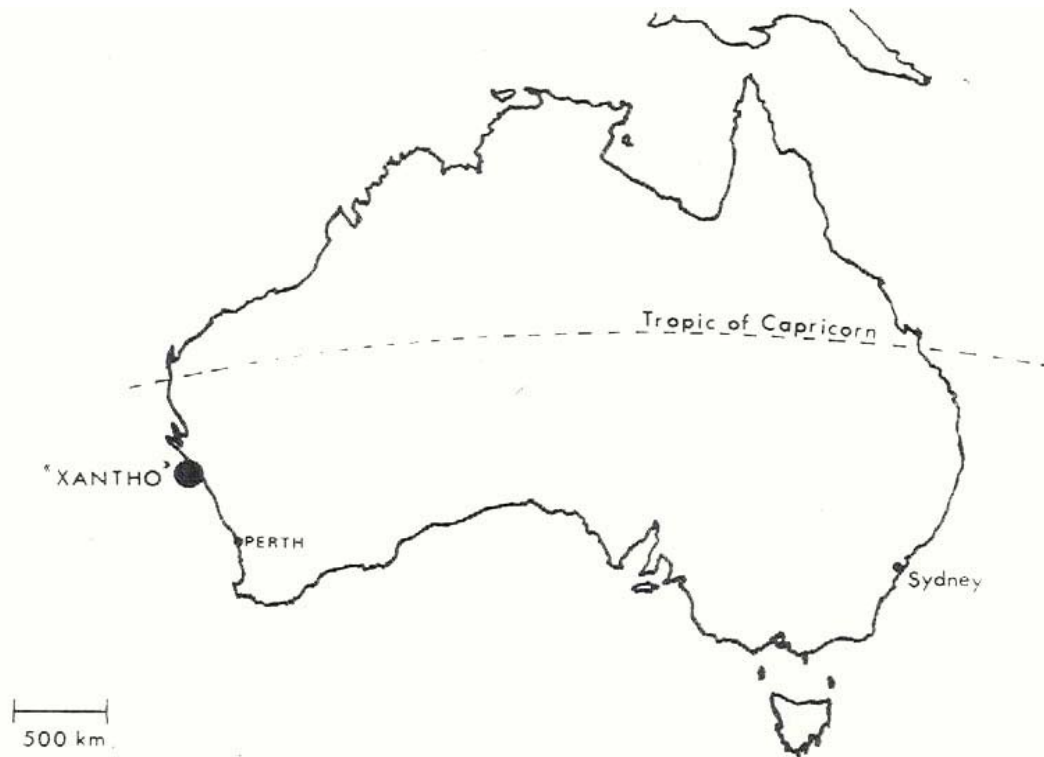


Fig. 1. Location of the wreck of the SS *Xantho*, 28°11.2'S, 114°14.1'E.

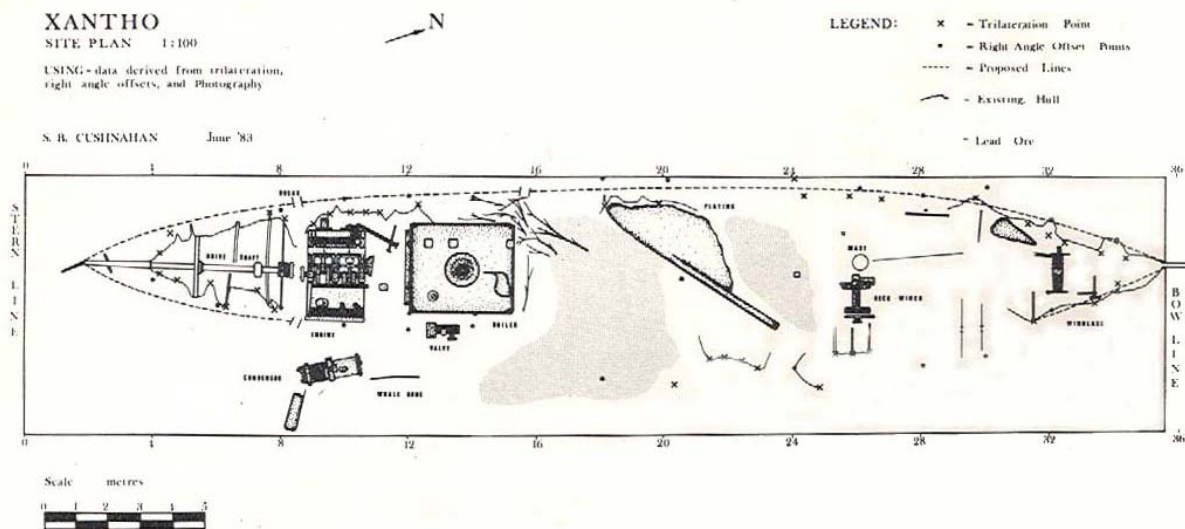


Fig. 2. Plan of the wreck site as examined during the pre-disturbance survey.  
The item noted as a condenser was later identified as a steam water heater.

## INTRODUCTION

Apart from their intrinsic merit as archaeological sites, shipwrecks provide a wealth of information about how the vessels and associated artefacts interact with the environment. In the tropical to sub-tropical waters of Western Australia very few wooden structures survive the ravages of wood-boring organisms; it is only when timbers are buried under coral debris, ballast mounds or sand that any significant structure remains. Examples of these environments are seen with the sites of the *Batavia* (1629), *Rapid* (1811) and *James Matthews* (1841) respectively. In order to properly understand the factors governing the degradation processes that occur on underwater sites, conservators must work in very close collaboration with maritime archaeologists. Conservation staff must dive and be able to perform a range of in situ measurements if the maximum benefit is to be gained from an excavation. As well as routine photographic documentation of the distribution of artefacts, the on-site recording of corrosion phenomena is vital since many degradation products undergo marked and irreversible changes once they reach the surface. The majority of conservation staff first see artefacts in an isolated context, often months after an excavation, and this presents many problems. Interpretation of corrosion and other degradation phenomena as well as the choice of the most appropriate treatment are fraught with difficulty if the archaeological context of the artefacts is not known.

Six years ago the wreck of the iron steamship *Xantho* was discovered by a group of volunteer archaeologists, some 550 km north of Perth, near the fishing settlement at Port Gregory (Fig. 1). A brief wreck inspection by a group of museum divers confirmed that it was the site of Western Australia's first screw-driven steamship which had sunk while carrying a cargo of the locally mined lead ore, galena. The 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 intrinsic merit in terms of pure scientific research but they are invaluable when applied to the excavation and conservation of historic shipwrecks.

This paper will report on all three phases of excavation from the pre-disturbance surveys in 1983 through to the final recovery of the *Xantho* engine. After the initial survey a cathodic protection system was installed to protect the historically significant steam engine from further corrosion. A second inspection showed that the site had been buried by four metres of sediment in only eight months. The third excavation season took place in April 1985 in an environment that had essentially returned to that which was initially observed. During the most recent season the engine was removed from the ship's structure and successfully brought ashore. It is now undergoing conservation treatment in the laboratories of the Western Australian Maritime Museum. Data obtained from other wreck sites will be utilized in the interpretation of phenomena on the *Xantho* site.

Detailed reports on the archaeology of the excavation of the *Xantho* site and the specialized techniques used in the recovery operation are to be found in reports by the project leader, and maritime archaeologist Mike McCarthy of the W.A. Maritime Museum (McCarthy, 1985).

### PRE-DISTURBANCE SURVEY - MAY 1983: Marine Biology

In terms of basic research into the microenvironment created by a shipwreck the *Xantho* appeared to be an ideal long-term experiment in marine fouling and artificial reef formation. Although completely submerged at all times, part of the wreck stood three metres above the seabed with large quantities of cast iron, steel, copper, brass and some white metal exposed to

colonization and subsequent growth by marine organisms. Since parts of the boiler and engine were well above the sand level, they provided a chance to look at the interaction of marine growth and metal corrosion. With the time span of more than 100 years it was an ideal opportunity for looking at the effects of long-term Interaction of wreck material with its environment. A plan of the wreck site is shown In Figure 2.

Initial inspection of the marine biology 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 carnivores feeding on the organisms that lived in the grass. The shipwreck site was a tunicate-dominated community with sedentary filter feeders being the major colonizing 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 -- 3.3 m) while large phacophylans were abundant in water deeper than 3.3 metres. The ship's boiler provided very good areas for studying the effects of the current on the marine growth since its long axis was essentially parallel with the direction of the strong current which ran at between 3 and 5 knots (1.5 - 2.6 m/sec). The boiler was approximately 3.2 m long, 2.8 m wide and 2.6 m high. A photograph of the boiler viewed from the port side is shown in Figure 3.

The observations on the biology of this structure are summarized below.

Top of boiler: surge perpendicular to current, approximately 0.5 m in amplitude. Apart from small tunicates living in the shelter of the remains of the steam dome, the top was encrusted with sponges and small green algae. Lower sections of the rounded top were colonized by large brown algae.

Forward side: periodic current fluctuations with a distinct demarcation of growth at 4.1 m depth. Above this line the growth was the same as on the top of the boiler but below, there were large tunicates (100 - 150 mm c.f. 70 - 100 mm in steam dome) and large upright sponges (50 - 100 mm high).

Port side: at depth less than 3.7 m the biological growth was similar to that of the top where the full force of the current is experienced. Between 3.7 m and 4.2 m depth there was a band of large brown algae down to the seabed at depth of 4.9 m.

Starboard side: the current runs along the plane of the face with large tunicates and small sponges covering the area between 3.3 and 4.0 m depth. The same organisms covered the remaining side to the sandy bottom at a depth of 4.7 m but with a much lower density. Above the 3.3 m level the growth was the same as at the top of the boiler.

Aft side: the water flow was irregular and the fauna was more varied than on the other parts of the boiler. The close proximity of the engine caused periodic backflows of water. The surface was covered with large brown algae from the 2.9 m to 3.7 m depth level where the sandy bottom had covered the lower parts of the fire box. Some feather worms and crinolds had colonized the interior of the exposed 70 mm diameter boiler tubes.

From the above observations it was apparent that the current exerts a marked effect on the growth of the marine organisms on the wreck. The strong current carried a large amount of weed and seaborne grit which gave a turbidity of 2.5 to 3.0 metres at best but often it was less than one metre. There appeared to be a marked change in the colonization of the boiler at a depth of  $4.2 \pm 0.1$  m, the significance of which was to emerge in the second season. 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 sea water was 8.1 with a water temperature of 23<sup>0</sup>C. No thermal gradient was observed during our measurements in the 3- 6 m range between 5<sup>th</sup> and 9<sup>th</sup> May. Although no direct measurements of dissolved oxygen were made it is reasonable to assume that because of the strong current and shallow depth it was close to 100% saturation.

## METAL CORROSION

Previous experience on sites such as the *Rapid* (1811) had shown that electrochemical measurements of parameters determining metal stability could be effected either on site or immediately the objects were raised (North, 1976 and MacLeod, 1981). The knowledge of parameters such as the pH and electrochemical potential of a metal combine to provide a very handy guide as to whether there have been changes in the microenvironment of a metal, whether or not it is actively corroding and whether any solid metal remains. Since the *Xantho* was the first iron steamship to be systematically examined by the Western Australian Museum, it was decided in conjunction with the project leader that an electrochemical survey of the site be made before any disturbance occurred. By examining the wreck prior to excavation we had access to a 100 year controlled corrosion experiment. Simulation of long-term marine corrosion phenomena in a laboratory situation is very difficult and there are many problems involved in the extrapolation of data from short-term studies (Taylor and MacLeod, 1985).

When metals are placed in oxygenated sea water they will begin to corrode. Positively charged ions are produced as the metal oxidizes and precipitated in the surrounding concretions or disperse in the sea. Each metal corrodes at a rate that depends on variables such as temperature, dissolved oxygen, salinity, water movement and the inherent reactivity of the metal in relation to water. Some metals react explosively with water, others corrode at a steady rate while yet other metals remain largely unaffected by immersion in water. Examples of these three categories are sodium, iron and silver, respectively. A convenient way of comparing such phenomena is to measure the voltage of a metal in equilibrium with a standard solution of its salts dissolved in water. Reactive metals give negative voltages, compared with the standard voltage of zero for hydrogen in an acid solution, whilst noble metals such as copper have positive standard voltages, E"s or standard reduction potentials.

Since we are concerned with metals in a marine environment, the solutions under consideration pertain more to sea water than to standard acid solutions. Because chloride ions alter the rates of many electrode processes (e.g. metal oxidation metal reduction) the standard electrode potentials (E<sup>0</sup>'s) of the metals in "standard sea water" are different from those in ordinary water. Iron and, less commonly copper and its alloys are often covered with a layer of marine growth which effectively places the metal in an environment which is different from normal sea water (North, 1976; MacLeod, 1982). Such environments tend to have a higher chloride concentration and lower pH and much lower oxygen concentration than ambient sea water since the concretions act in many ways as a semi-permeable membrane which inhibits rapid transport of some ions and gases.

When a metal is corroding, one of two processes limits the rate of the corrosion reaction: it is either the rate of the cathodic process (which is commonly called oxygen reduction) or the rate of the anodic process (metal dissolution). Other cathodic processes include the reduction of hydrogen ions to hydrogen gas and the reduction of sulphate to sulphide ions. For most cases

involving concreted metals the rate of oxygen reduction is the controlling factor that determines how fast the object will corrode. The voltage of a metal object in the sea will be dependent on how fast the metal is corroding and this is interdependent on the pH of solution adjacent to the corroding object. If we have a knowledge of the pH and the voltage of the corroding metal (commonly called the corrosion potential,  $E_{\text{corr}}$ ) we can tell whether the metal is immune (cannot corrode), is passive (very slow corrosion) or if it is actively corroding. Since the voltage is dependent on both the metal oxidation and cathodic reduction processes the voltage is also known as a "mixed" potential. Such electro-chemical data are conveniently presented in a Pourbaix diagram (Pourbaix, 1974).

## **XANTHO DATA**

The corrosion potentials were measured In situ using a high impedance digital multimeter (Fluke 8010A), a platinum electrode (0.8 mm thick) housed in an epoxy body and a silver/silver chloride reference electrode (Titron model No. 211). Subsequent measurements were performed using a different silver chloride reference electrode (DIMET). Sea water was used as the reference solution. The procedure consisted of drilling into the concretion (using a ¼" masonry bit and a hand drill) and placing the platinum electrode into the hole while pressing firmly to establish good electrical contact; the reference electrode was placed adjacent to the concreted metal surface and the voltage measured. For the resistance survey the reference electrode was replaced with a stainless steel probe (see Fig.4) and both were brought into contact with the holes drilled in the metal concretion.

A summary of the results of the survey are shown in Table I and also in a diagrammatic way in Figs. 5 and 6 which show the Pourbaix diagrams for Iron and copper in sea water. Although in situ pH measurements were not done on the wreck material, we have estimated the pH of the metal under concretion on the basis of our previously published data on iron and copper-based concretions (North, 1976, MacLeod, 1982). When the iron concretion was being drilled bubbles of escaping gas were occasionally observed - the gas is mainly hydrogen and light-weight hydrocarbons that are formed as a result of the corrosion process (North, 1982). Inspection of the Pourbaix diagram shows that the potential of the frame plates lies on the hydrogen discharge line, viz. at such potentials and pH, water is in equilibrium with one atmosphere of hydrogen gas. Seventeen of the twenty-five sites measured had a corrosion potential of  $-0.268 \pm 0.004$  volts vs NHE (or  $-.0539$  vs AgCl seawater); in effect this shows that they are all in essentially the same corrosion microenvironment. From the observed relationship between corrosion currents and voltage in laboratory experiments, the standard deviation of 6 mV means that the rates of corrosion are within thirty percent of each other. The difference of 113 mV between the corrosion potentials of the deck winch and the frame plates near the stern reflects a ten-fold difference in their relative corrosion rates. The value of  $-0.103$  volts for the windlass is typical of potentials where no solid metal remains and this was indicated when the drill bit penetrated to a depth greater than 100 mm without striking solid metal.

All the potentials observed for the non-ferrous fittings showed that they are all in the immune (for copper and brass) (Fig.6) or passive zones (white metal on crankshaft bearings). The corrosion potentials of the brass steam cocks and valves are largely determined by the iron corrosion potentials since the objects are in electrical contact with the iron metal which has a much larger mass and surface area. Although the copper and iron fittings on the engine have the same potential the results are different; copper and brass will not corrode while iron is actively

corroding. The concretion layer observed on the brass and copper fittings was a few mm thick and consisted of a dense white calcareous deposit. Because of the galvanic protection provided by the corroding iron, the copper based alloys act as cathodic sites in the corrosion cell and this causes the surface pH to increase and inorganic calcium carbonate as calcite/aragonite precipitates on the metal. Once this protective" layer of  $\text{CaCO}_3$  covers the biologically toxic metal corrosion products, the surface is then subject to normal colonization by marine organisms. The  $\text{CaCO}_3$  layer appeared to act as a barrier to oxygen diffusion since under its protection some of the  $\text{Cu}_2\text{O}$  on the metal surface had been converted to  $\text{Cu}_2\text{S}$  through the action of sulphate reducing bacteria. The less negative potential for the copper tubes and case on the steam water heater is simply due to the relatively small mass of iron attached to the copper tubing which has a large surface area.

Although the corrosion potential of the white metal bearings on the crankshaft is -0.268 volts vs NHE is outside the immunity range for lead it is in a region of stability of passivation through lead sulphate (anglesite) formation. On- site inspection suggested that the 2.5 mm film covering the bearings was a mixture of anglesite and calcite ( $\text{PbSO}_4$  and  $\text{CaCO}_3$  respectively).

## SUMMARY

The electrochemical survey on the metal structures of the shipwreck gave us three parameters that are directly related to the condition of the underlying metal, i.e. corrosion potential, presence of entrapped gases and the depth to solid metal. The engine and the boiler are in relatively good condition with low potentials, no significant gas evolution and solid metal relatively close to the original surface. The non-ferrous components of the engine and boiler are in excellent condition with potentials too low for active corrosion. The hull remains were in a fair condition with the amount of corrosion attack being higher in the forward areas than in the stern. The windlass is very badly corroded with the concretions alone retaining its shape - very little solid metal would remain. Similarly the iron steam fitting attached to the copper coils appears to be in an extensively corroded condition.

## MINERALOGY OF ORE CARGO

Samples of the galena (lead sulphide) ore were taken for examination under a scanning electron microscope. Mineralogical analysis of the original high purity ore showed that small amounts of minerals other than galena were associated with the deposit, namely lead carbonate, zinc blende, iron pyrites, blue slaty clay and quartz (Wilson, 1926). Since there were no arsenic or mercury compounds in the galena it is unlikely that there was any marked influence on the marine ecology from material leached from the minor compounds of the galena. The SEM micrographs of the galena samples recovered in the pre-disturbance survey (Fig.7) showed that some of the mineral had oxidized. Lead had migrated out of the galena matrix to the surface where it was deposited in two forms. The spiky crystals are phosgenite ( $\text{Pb}_2\text{Cl}_2(\text{CO}_3)$ ) and the plate-like crystals growing into cubes are the hydroxy carbonate hydrocerussite  $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$  (Thornber, 1985). A sample of ppm lead while a iron concretion downstream from the mound of galena had 162 sample of concretion from *Vergulde Draeck* (1656) which carried general cargo, was  $61 \pm 6$  ppm. The significance of the solubilization of lead from the cargo (Mann & Deutscher, 1980) on both the corrosion rates and marine biology is yet to be determined. The amount of lead in the concretion from the *Vergulde Draeck* (1656) site probably reflects uptake of lead in seawater by marine organisms such as coralline algae (Sterner and Nickles, 1974).

## **EXCAVATION AND INSTALLATION OF CATHODIC PROTECTION SYSTEM**

In order for the archaeologists to make detailed drawings of the historically important engine, it was necessary to remove a lot of the living marine growth from the engine. Only loosely attached material was removed since the hard calcareous concretions over steel and cast iron protects the underlying metal from accelerated corrosion (North, 1982). The surface cleaning also revealed many bright brass fittings which would attract the attention of a sports diver. The electrochemical survey had also resulted in many small holes having been drilled into parts of the structure. It was decided to install a sacrificial cathodic protection system to protect the engine from further corrosion.

In general terms a sacrificial cathodic protection system consists of a highly reactive disposable metal which is in electrical contact with a less reactive metal. This forms a galvanic couple with the more reactive (and expendable) metal suffering increased corrosion attack and the less reactive metal, usually steel, being protected against corrosion. Details on cathodic protection are readily available in standard text books on the subject (Shrier, 1976).

There are several desirable effects that could be obtained from installation of a cathodic protection system for the *Xantho* engine. Apart from corrosion control the action of cathodic protection generates alkali at the metal-seawater interface and thus raises the pH of the sea water which causes calcium carbonate to precipitate. The white calcareous deposit would hide bright copper/copper alloy fittings under a paint-like layer and so help to protect them from theft by divers. The cathodic protection system would also tend to block up any of the holes drilled during the potential survey. Under normal site conditions copper artefacts tend not to be concreted, owing to the toxic nature of their surface. Under cathodic protection the toxicity of the metal is greatly diminished and colonization by marine organisms is not impeded (MacLeod, 1982).

## **DESIGN AND INSTALLATION**

In order to be cathodically protected, the object must be in metal-to-metal electrical contact with the anode. An electrical continuity survey was performed by measuring the electrical resistance between different points on the engine, boiler and drive train. Because of the electrical conductivity of sea water it is difficult to establish which pieces of metal are in metal to metal electrical contact since the value of a metal/sea water/metal pathway may also be very small. There is also the problem of making good contact between components and so one of the resistance probes was always in contact with either copper, brass or white metal in an attempt to minimize such problems. The survey showed that the engine formed a single conducting unit which was also electrically bonded to the propeller shaft. Most of the copper pipe work was in electrical contact with the engine but there was no apparent metal-metal contact from the engine to the hull remains or to the boiler or the steam water heater.

It was decided to install two protective anodes on the engine. Each anode consisted of a 2 kg magnesium anode welded to a 25 kg aluminium anode. Sufficient cable was used to place the anodes outside the hull remains and at a sufficient distance from the engine (3-4 m) to give a good current spread. The anode cables were welded to a clamp system which was bolted onto the propeller shaft and onto a white metal bearing on the crankshaft. Each clamp was individually designed to fit the particular part of the engine. Before attaching the clamps each point was deconcreted back to the original metal. No apparent problems occurred during the installation.



## SITE DISTURBANCE - 1984

As a result of the initial survey the boiler and the engine had been cleaned of the bulk of the marine growth and a cathodic protection system had been installed on the engine. It was planned to check the regrowth on the engine and the functioning of the cathodic protection system after eight months of operation. It was presumed that the warmer spring and summer months of October through to January would have seen significant recolonization of the engine. Since the boiler and engine were not electrically connected a comparison of the regrowth on these objects would have given information on the effect of cathodic protection on the marine ecology. Physical inspection of the site showed that the seabed conditions had altered markedly since the pre-disturbance survey.

The whole engine was covered in sand and only the top 1.5 m of the boiler was exposed. Skeletal remains of surpulid worms, coral, bryozoans and assorted molluscs were still attached to the surfaces of the boiler but no animals remained. The top 0.9 m of the boiler had an extensive growth of green filamentous algae with some small brown and white banded fan seaweed and light brown banded ribbon seaweed approximately 75 mm long. The lower 0.6 m of the boiler had only a small growth of green filamentous algae. These observations, when combined with the reports of local divers, suggest that until a few weeks before our return trip the whole site had been completely buried for some time. The current began to scour the site and exposed the top 0.9 m of the boiler in the last week of 1983 and further began to clean away the next 0.6 m in the first two weeks of January 1984. Periodic burial is the obvious explanation for the marked change in colonization of the boiler at the 4.0 + 0.2 m depth that was observed in the initial survey (see Fig.3). Any comparison of regrowth with and without cathodic protection was made impossible by the burial. After removing the metre-thick overburden of sand from the engine (using water dredges manned by the archaeologists) corrosion potential measurements were made on the anode attachment bracelets. The bracelet on the crankshaft bearing was only -0.450 volts vs hydrogen whereas effective cathodic protection is only obtained with voltages as low as - 0.540 to - 0.610 volts vs SHE (Wilkins, 1982). The bearing itself had a potential of - 0.264 volts which indicated that there was poor electrical contact between the bracelet and the object (see Table II). Although the 5 mm thick white calcareous deposit on the bracelet indicated that the anodes had been working, it was readily apparent that they were not functioning under several metres of sediment. The bracelet on the propeller shaft showed even less apparent protection than the fitting attached to the crankshaft.

The following day, attempts were made to excavate the anodes but the fine sand gave way, only one metre down below the current seabed, to a mixture of fine sand and clay. This matrix could only be shifted by breaking it up with a geopick. Equipment and personnel constraints meant that the anodes had to remain buried. Aluminium anodes are designed to function in open sea water and although they can perform satisfactorily under one metre of fine sand they cannot function under a metre of clay which is overlaid with three metres of sand.

The apparently anomalous marine ecology of the *Xantho* site as first observed can readily be understood in terms of the burial phenomena described above. 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. Apart from killing all the colonizing marine animals, the burial causes the site to change from an aerobic to an anaerobic one. The mixed cuprite ( $\text{Cu}_2\text{O}$ )/chalcocite ( $\text{Cu}_2\text{S}$ ) patina observed under the thin layer of calcite on some of the brass pressure relief valves (on top of the trunks) is readily

explained by periodic changes from aerobic to anaerobic environments.

Examination of a polished specimen of copper wire from inside a water spray device, found lying proud of the seabed in the 1979 wreck inspection tour, showed up a typical banded formation with layers of the copper sulphide chalcocite ( $\text{Cu}_2\text{S}$ ) (Fig.8). Such banding is consistent with the periodic exposure to anaerobic/aerobic conditions over the last 110 years that would occur each time the site was buried/exposed.

Since the pre-disturbance survey had indicated that the engine appeared to be in a remarkably good condition, the archaeologist in charge of the project decided to attempt to recover the engine for the purposes of research and display. As the only remaining example of the first mass-produced marine steam engine, the *Xantho* is of prime importance to industrial archaeologists. In order to minimize any damage to the site, excavations of the seabed were made only in the vicinity of the four steel bearers on which the engine was supported. A thermal lance was used to cut through the badly corroded iron beams and this let the engine settle onto a support system of 100 mm square blocks. Details of this phase of the excavation have been reported elsewhere (McCarthy, 1985). The engine was partly disguised with rocks in an attempt to make the structure less obvious when viewed from the surface.

#### **RECOVERY OF THE ENGINE - APRIL 1985**

Before commencing any dredging operations the site was inspected and shown to be in a similar physical condition to that found in the initial survey in May 1983, except that the current was greatly diminished. Corrosion potential measurements showed that no change had occurred in the microenvironment of the metal in the boiler. The fact that the potentials were the same indicates that the concretion layer tends to insulate the metal from changes at the sea water--concretion interface (see Table II). The water temperature was  $21.5^\circ\text{C}$  and the salinity at the 7 m level was 37.3 parts per thousand which is essentially the same as during the initial inspection. The areas of the brass steam valves and tool box by the propeller shaft that had been exposed to bare metal were repatinated with a thin layer of calcareous material. Potential measurements showed that they had the same potentials as the iron objects in the immediate vicinity. The deposition of calcium carbonate on the exposed areas of the brass fittings was more probably due to the protection gained from the iron itself rather than from the sacrificial anode system. Measurements of the corrosion potentials of the anode bracelets showed a small improvement in the propeller shaft potential (towards protection) but a lowering of the extent of protection on the crankshaft bearing when compared with the previous readings fifteen months previously (see Table II).

During the clearing of the surrounds of the engine, the anaerobic nature of the seabed material was noted through the rapid tarnishing of sterling silver rings on the divers' hands and poisoning of the silver/silver chloride reference electrode with hydrogen sulphide. The regrowth on the boiler was about half as intensive as during the initial inspection of the site which may indicate that we had seen two years' marine growth in the first instance. Typical fouling rates in shallow and warm coastal waters can be up to  $20 \text{ kg/m}^2/\text{year}$  depending on current, supply of nutrients and the season (De Palma, 1982).

The team leader, two riggers, one photographer and a video cameraman formed the crew that raised the engine from the seabed and recorded the exercise. Details of the techniques used in raising the 7.8 tonne artefact can be found in forthcoming reports - the basic procedure consisted

of attaching several air bags to the engine using heavy-duty, 5 cm thick, synthetic rope and broad-woven lifting strops with lifting capacities of 1 tonne per thickness. The engine was cushioned from localized lifting pressure by distributing the load with sandbags (Fig.9). After clearing the site, the engine was towed to a steel sled in shallow water. The sled was then raised and attached to the engine before both were gently lowered to the seabed by deflating the lifting bags. One day after removing the engine, and immediately prior to its being brought onto dry land, the corrosion potential was remeasured at the same reference point. The voltage was the same as found on the initial survey (within experimental error) and 121 mV more positive than before the cable from the anode was cut (see Table II). Although the anodes were not operating at full efficiency, the observed swing of 121 mV in the steel potential would have caused a reduction of approximately 90% in the iron corrosion rate, i.e. the anodes gave effective protection to the engine. The potential of the boiler and the copper steam water heater were remeasured on the main site and found to be unchanged by the removal of the engine, i.e. we were able to demonstrate that extraction of the engine caused no immediate changes in the microenvironment of the remaining artefacts.

The sled and engine were brought ashore by pulling the sled along the seabed with chains attached to a bulldozer and an articulated front- end loader. The sled was dragged along the beach and up onto level ground where it was secured. After being photographed, the engine was saturated with fresh water then covered with a layer of sodium carbonate (dense soda ash) before being wrapped up in wet hessian. The hessian was covered with a layer of a polymeric gel material (Erosel, a polyamide) which effectively stopped the engine drying out. The hessian was covered with a heavy- duty black plastic membrane and this was overlain with a tarpaulin. Despite the strong easterly winds and high daytime temperatures (30°C), the engine remained wet between the daily "baths" of fresh water\* which was poured over the hessian. Although the hessian would tend to dry out, the gel coating stopped any significant evaporation of the underlying material and so maintained a moist alkaline environment for the engine. The use of sodium hydroxide solutions was ruled out because the brass and white metal components would have corroded. The health hazard created by a strongly caustic solution oozing onto a public car park also precluded its use at the holding site. Before transporting the engine to Perth it was again uncovered and photographed using specialized survey equipment (stereographic photographs from four sides using full- sized glass plates) so that a three dimensional record would be retained. In the event of damage to the engine on its road journey. After five days on land the engine was lifted by a crane and placed on a bed of sandbags over the forward section of an articulated heavy haulage vehicle. A plastic membrane placed under the bags was sealed with tape to a similar covering over the engine. Before the final seams were taped, 200 litres of fresh water was poured into the giant plastic bag - this kept the engine wet until we reached our overnight stop. The following day more water was added for the second leg of the 550 km trip to the laboratories in Fremantle. Inspection of the engine at the end of the road trip showed no apparent damage to the protective concretion layers and there were no tell-tale red-brown rust spots on the artefact which would have indicated fresh corrosion attack. The engine was lifted by a crane and lowered into a specially-built steel treatment tank some 3 m x 3.5 m x 2 m deep.

The storage, deconcretion and conservation of the engine will be reported in later publications. Some idea of the scale of the exercise is seen in the quantities of materials involved in the treatment. A total weight of 1.8 tonnes of concretion has been removed and after only three

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\* Although in limited supply the local tap water was used to wet the engine; the chloride level was 897 ppm

months of treatment more than 10 kg of chloride ions have washed out from the engine into the 14 m<sup>3</sup> of 1 wt% sodium sesquicarbonate solution. Test drillings into the cast iron fittings show corrosion depths of between 1 mm and 3.5 mm which correspond to corrosion rates of 100 to 32 µm/year. The average corrosion rate for iron in a marine environment is 100µm/year with a range from 25 to 190 µm/year (La Que, 1975) so the observed values for the engine fall within the range of other long-term studies. More research is needed to establish whether or not the engine was protected in part by preferential corrosion of the hull plates and other parts of the ship's structure. The cyclic changes of the site from aerobic to anaerobic conditions is probably the most significant factor in determining the extent of corrosion on the engine.

## **SITE PROTECTION**

It is planned to raise the stern section of the hull in 1986. The rudder, propeller and two frames being removed from the site will be transported in a similar fashion to the engine. Since the stern is one of the strongest parts of a steam ship, its removal could cause the collapse of any remaining structure. To prevent such an occurrence, concrete sections will be laid in situ to act as a retaining device for the hull. Sacrificial anodes will be attached to the remaining sections of the hull to minimize further corrosion. Concretion samples will be taken from the areas upstream and downstream from the lead ore and analysed to further clarify what effects the galena has had on the corrosion and colonization processes. The site will be periodically inspected by members of the excavation and conservation team to see what effects the removal of the engine has on the nature of the site. Since the massive boiler bears the brunt of the current, it is anticipated that the sections of the wreck aft of the engine will not be adversely affected by this first stage of excavation. Sufficient ship's structure remains for the site to be immediately identifiable as that of the SS *Xantho*. Souvenir clothing and spoons, marked with the excavation logo, are available at the local shop and this practice has resulted in a greater public awareness of the site. The local fishermen now keep a watchful eye on the site to protect it from being damaged by divers.

## **CONCLUSION**

The work on the *Xantho* has shown how a wreck site can be managed so that the maximum benefit can be obtained from an excavation.

The close cooperation between maritime archaeologists, conservators, biologists and corrosion scientists enabled a pre-disturbance survey to be carried out prior to any effective excavation. On the basis of measurements made during the survey, it was decided to raise the historic, horizontal trunk steam engine and to transport it over 550 km to the laboratories for treatment. A sacrificial anode system was installed to protect the engine from further corrosion whilst treatment facilities were being constructed. Dramatic changes in site conditions resulted in a poorer performance by the anode system than we had hoped for but measurements showed that the system had worked. Monitoring of the site during and after excavation of the engine showed that the operation had been effected without any damage to the engine itself or to the remaining structures. The experience gained with the *Xantho* has already been applied to excavations in remote locations where a large anchor from HMS *Sirius* (1790) was protected by sacrificial anodes whilst awaiting construction of a treatment tank (MacLeod, 1985 b). The possibility of treating large metal structures "in situ" has major implications for preserving underwater archaeological sites.

## **ACKNOWLEDGEMENTS**

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TABLE I: Corrosion potentials of objects on the SS *Xantho* site, before disturbance.

	$E_{\text{corr}}^+$ , volts vs SHE	Observations
Propellor shaft, crankshaft, plating near stern, engine block connecting rod, stuffing box, etc.	$-0.268 \pm 0.004$	Some gas evolution on penetrating 22 mm concretion
Boiler	$-0.270 \pm -0.283$	Concretion 4-12 mm
Deck winch	-0.216	Gas evolved, concretion 50 mm
Windlass	-0.103	No solid metal, drill in 110 mm
Brass steam cocks	-0.266	Very thin concretion
Frame plates	-0.280	Gas bubbles
Steam water heater (copper coils)	-0.163	Not much solid iron

<sup>+</sup> Potentials were measured with a platinum electrode using a Ag/AgCl sea water reference which was calibrated using the voltage of the platinum electrode in a pH 4.0 solution saturated with quinhydrone.

TABLE II: Corrosion potentials of the *Xantho* engine before and after excavation.

Object	Corrosion potential, volts vs SHE*			Post excavation
	Pre-disturbance	Anode connected 8 months	23 months	
Propellor shaft	-0.269	-0.295	-0.319	-
Crankshaft bearing	-0.268	-0.450	-0.395	-0.274
Boiler **	-0.270	(-0.270)	(-0.270)	(-0.272)
Copper / iron steam water heater	-0.163	-	-0.159	-0.158

\* Voltages were measured using Ag/AgCl sea water reference electrodes which were calibrated against a platinum electrode in a quinhydrone solution at pH 4.0.

\*\* Potential measurements on the boiler were unaffected by the sacrificial anodes since it was not in direct electrical contact with the engine.

## BIBLIOGRAPHY

- De PALMA, J.R.. "Horizontal and vertical distribution of fouling in the world ocean." *Fouling and Corrosion of Metals in Sea Water*, ed. J. Mauchline, pp. 7-15. Scottish Marine Biological Association, 1982.
- La QUE, F.L. *Marine Corrosion*. New York: John Wiley and Sons., 1975.
- MACLEOD, I.D. and N.A. NORTH. "Three hundred and fifty years of marine corrosion In Western Australia." *Corrosion Australasia* (1980) 5(3):11- 15.
- MACLEOD, I.D. "Shipwrecks and applied electrochemistry". *J. electroanal. Chem.* (1981) 118:291-304.
- MACLEOD, I.D. "Formation of marine concretions on copper and its alloys." *Int. J. Naut. Arch. & Underwater exploration* (1982) 11(4):267-275.
- MACLEOD, I.D. (a) "The effects of concretion on the corrosion of non ferrous metals." *Corrosion Australasia*, 101(4) (1985) (in press).
- MACLEOD, I.D. (b) Conservation report - 1985 HMS Sirius expedition, Norfolk Island (unpublished report, 1985).
- MANN, A.W. and R.L. DEUTSCHER. "Solution geochemistry of lead and zinc in water containing carbonate, sulphate and chloride ions." *Chemical Geology* (1980) 19:293-311.
- McCARTHY, M. The excavation of the SS Xantho - W.A. Museum Report (in press, 1985).
- NORTH, N.A. "Formation of coral concretions on marine iron." *Int. J. Naut. Arch. & Underwater exploration* (1976) 5(3):253-258.
- NORTH, N.A. "Corrosion products on marine iron." *Studies in Conservation* (1982) 27:75-83.
- POURBAIX, M. *Atlas of electrochemical equilibrium in aqueous solutions*. 2nd English ed. Texas: NACE and Brussels: CEBELCOR, 1974.
- SHRIER, L.L. "Cathodic and anodic protection." In *Corrosion* (1976) 11(2). London: Newns - Butterworths.
- STENNER, R.D. AND G. NICKLES "Distribution of some heavy metals in organisms in Hardanger fjord and Skjerstad fjord, Norway." *Water. Air Soil Pollut.* (1974) 3:279-291.
- TAYLOR, R.J. and I.D. MACLEOD. "Corrosion of bronzes on shipwrecks - a comparison of corrosion rates deduced from shipwreck material and from electrochemical methods." *Corrosion* (1985) 41(2):100-104.
- THORNBURGER, M.R. "Supergene alteration of sulphides, VII. Distribution of elements during the gossan forming process." *Chemical Geology* 34 (1985) (in press).

WILKINS, N.J.M. "The cathodic protection of metals in sea water." *Fouling and Corrosion of Metals in Sea Water*, ed. J. Machline, pp. 96-116. Scottish Marine Biological Association, 1982.

WILSON, R.C. *The Northampton Mineral Field*, p. 17. Perth: Western Australia Govt. Printer, 1926.





Fig. 3. The *Xantho* boiler as viewed from the port side during the pre-disturbance survey. The inside measurement of the square grid scale against the boiler is 1.0 metres. Photo: Pat Baker.



Fig. 4. Drs. MacLeod and North measuring corrosion potentials on the *Xantho* site during the pre-disturbance survey. The concretion on a piston is being drilled so that the potential measurement on the underlying material can be made.

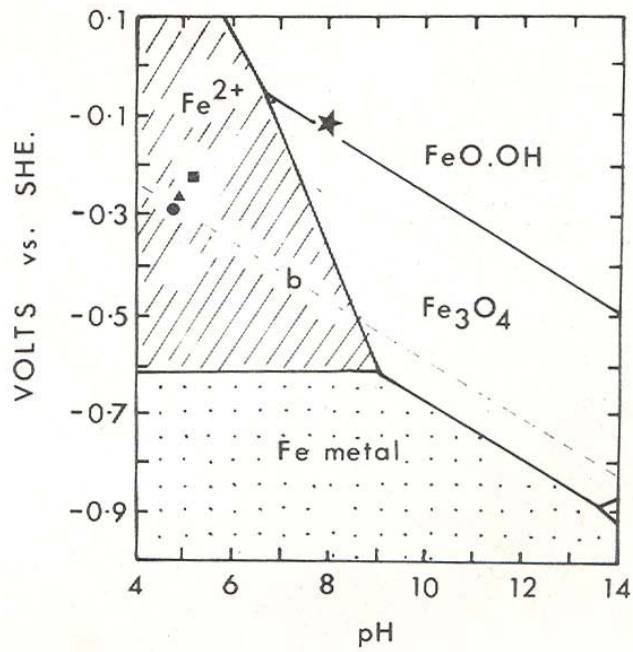


Fig. 5. Pourbaix diagram for iron in equilibrium with a  $10^{-6}$  M  $\text{Fe}^{2+}$  solution showing on-site corrosion potentials for various parts of the engine. ★ windlass, ■ deck winch, ▲ mean potential of sixteen objects, ● frame plates, b represents the equilibrium line for water and one atmosphere of hydrogen gas.

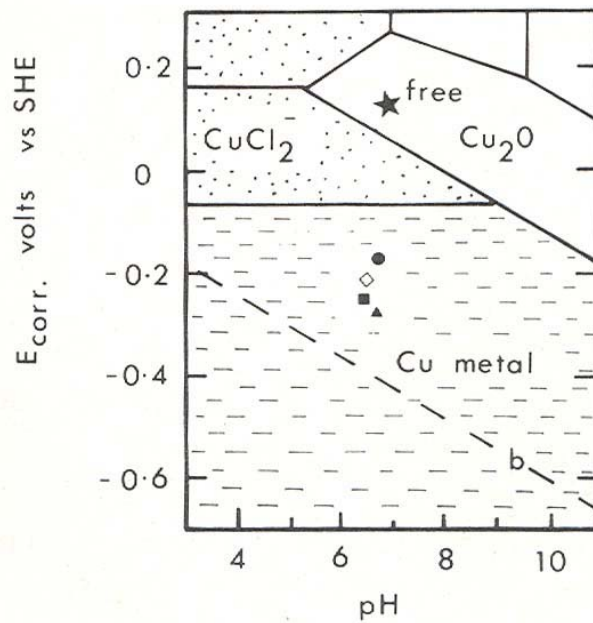


Fig. 6. Pourbaix diagram for copper in sea water in equilibrium with a  $10^{-6}$  M copper solution. The on-site corrosion potentials illustrated are for ★ free copper pipe between the boiler and the engine, ● unidentified copper fitting on engine, ◇ steam pipe on water heater, ■ small copper pipe on engine and ▲ for brass steam cocks attached to the engine.

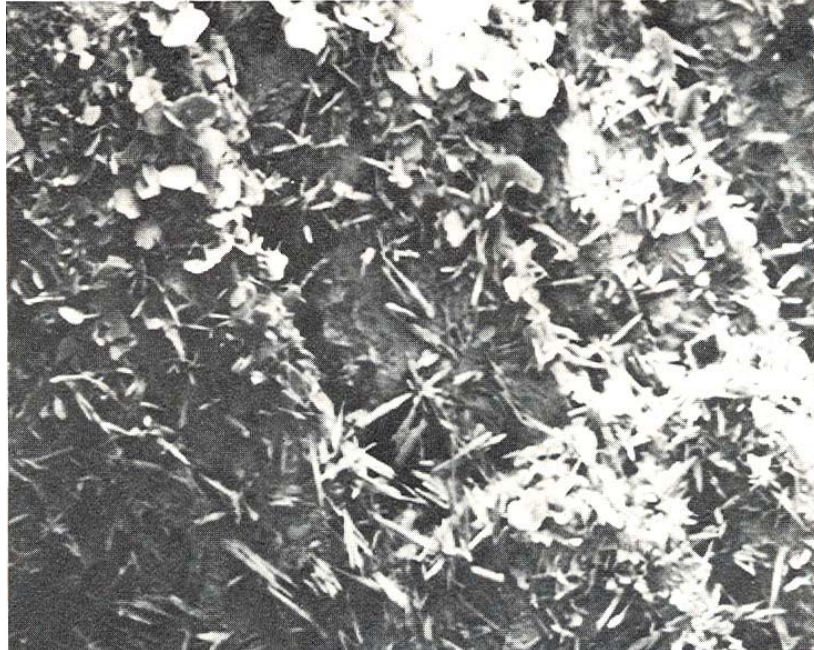


Fig. 7. Scanning electron micrograph of the oxidized galena ore. The spiky crystals are phosgenite  $Pb_2Cl_2(CO_3)$  and the plate-like crystals are hydrocerussite,  $Pb_3(OH)_2(CO_3)_2$  which overly the present galena crystals. Full width of the photograph is  $750\mu m$ .

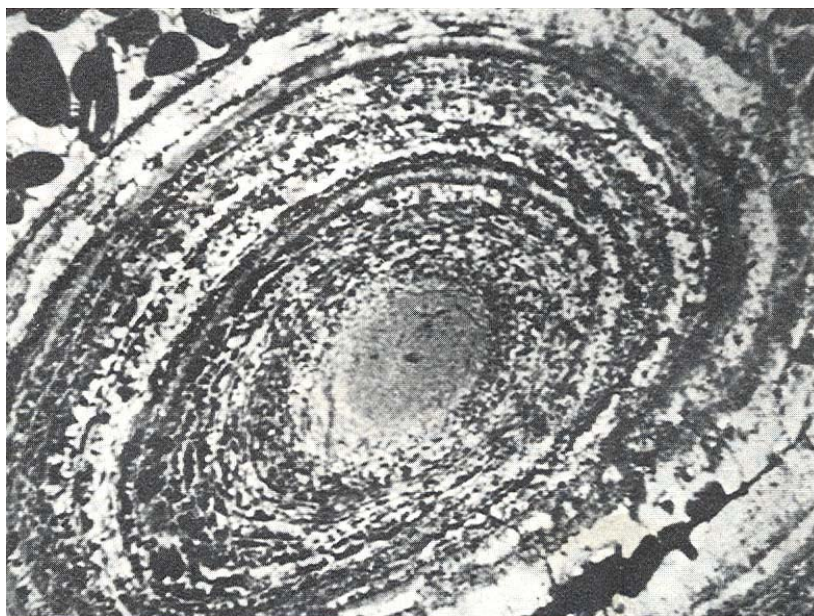


Fig. 8. Scanning electron micrograph of a mounted cross-section of mineralised copper wire. The light grey material is the copper mineral chalcocite ( $Cu_2S$ ) while the black material is predominantly calcium carbonate. The banded formation is centred round a core of residual copper oxide. The full width of the photograph is  $2.6mm$ .



Fig. 9. Raising the *Xantho* engine. Photo: Pat Baker.