

Conservation of the SS Xantho

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Abstract

The conservation of a massive 5½ tonne marine steam engine from the wreck of the SS Xantho (1872) has provided many examples of excellence in quality engineering from the early Victorian period. The use of traditional electrolysis in caustic solutions has presented significant problems, with large areas at the square edges of the curved cast iron sections of cylinders, flanges and pumps exfoliating. Analysis of the deterioration patterns has concluded that prolonged exposure to fresh water during periods of deconcreting the massive object caused interfacial corrosion at the boundary between the graphitised section and the phases containing residual metal. Alternative conservation management procedures have been recommended to prevent such incidents happening with similar projects involving the treatment of massive marine cast iron structures. The use of *in situ* pre-treatment with sacrificial anodes is strongly recommended prior to the recovery of the objects.

Introduction

The foundations for this project began in 1980 when conservators of the Western Australian Museum were teaching conservation, theory and practice as part of the Curtin University Maritime Archaeology Diploma. One of the students was Mike McCarthy, a practising maritime archaeologist from the Department of Maritime Archaeology of the Western Australian Museum. He was keen to see if Neil North's theories on iron corrosion in seawater could be applied to the management of an iron shipwreck. The 1979 discovery of the wreck of Western Australia's first iron steamship at Port Gregory provided Mike McCarthy and Neil North's team of conservators with an opportunity to perform a controlled *in situ* study of an iron shipwreck before any major disturbance took place. This approach was indeed novel for no other maritime wreck site in Western Australia had been studied in any detail before archaeological intervention took place. The results of the biological pre-disturbance survey and the physical, chemical and electrochemical surveys (McCarthy 1988 and MacLeod et al. 1986) saw a much deeper understanding emerge of the various forces which were controlling the deterioration of the vessel. The identity of the wreck was not in question, since archival sources showed it was the SS Xantho, built in 1848 in Dumbarton, Scotland and converted from a paddle steamer to a screw driven vessel in 1871, with an 1861 engine by Penn & Son of Greenwich (Kimpson & McCarthy 1988). Although salvaged at the time, significant portions of the original

structure remained when the site was discovered in 1979. The recovery of the engine from the historic steamship Xantho (1872) has provided conservators and maritime archaeologists with a real challenge. The details of how the 7½ tonne concreted mass of the steam engine of the SS Xantho was transformed into the original sections has been reported in terms of the removal of 48.1kg of chloride ions in seven years of active conservation treatment (MacLeod 1992). The amount of chloride ions in the corroded engine are listed in Table 1 which shows the way in which the values changed during the course of the conservation treatment program. The extracted chlorides amount to only 1.00 wt% of the initial total artefact weight, but the 2,544kg of marine concretion and corrosion products which have also been removed (North 1976). The Xantho project has led to a new understanding of the interaction of iron shipwrecks with their microenvironment, and has seen the beginning of *in situ* conservation processes (MacLeod 1987). In order to understand what has happened to the once "pristine" engine it is vital that the nature of corroded, concreted wrought iron and cast iron with numerous parts made of copper piping, brass and bronze valve fittings attached to it. The presence of the non-ferrous materials would have exacerbated the corrosion differences between wrought and cast iron sections.

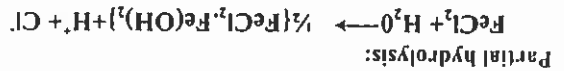
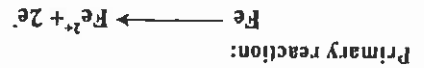


Table 1. Chloride ion concentrations in various iron fittings as a function of treatment time.

Date	Section	Chloride (wt.%)
May 1983	Wrought iron plate near stem	1.71 max 0.62 mean
June 1983	Concreted eccentric solution	0.922
November 1987	Drive shaft: d _p 5 mm	0.081
November 1987	Counter balance	0.073
November 1987	Wrought iron midline support	0.025
November 1987	Wrought iron plate	0.041
November 1987	Aft starboard piston (freshly exposed)	0.462
November 1987	Aft lower cylinder case (freshly exposed)	0.351

Corrosion Mechanisms for Concreted Marine Iron Objects

At the time of inspection, when the wreck had been corroding for more than one hundred years, the microenvironment adjacent to iron surfaces had become significantly more acidic and chloride-rich than the surrounding marine environment (North 1976 & North 1982). The increased acidity is due to hydrolysis of the metal ions; the acidity increases until it reaches a quasi-equilibrium state that is commensurate with the average long-term corrosion rate (MacLeod 1995). The basic equations describing the initial corrosion reaction and the subsequent *in situ* hydrolysis are:



This encapsulation process of marine concretions formation begins the separation of 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 1989a). The corrosion process results in the inward diffusion of chloride ions from the sea through the marine growth to the corroding metal (MacLeod 1989b). Previous experience of the post-excavational problems of exfoliating cannon balls from the Batavia (1629) wreck had shown that it was

important to avoid removal of the concretion without prompt immersion into alkaline media commonly used for storage and conservation treatments (Carpenter, J. 1992, pers. comm.). Once the caustic solutions have permeated the corroded matrix, the iron is in a passive corrosion state i.e. it is corroding at a much slower rate than would be found in the acidic and oxygen rich environment that exists after recovery from the seabed. To minimise such problems, the engine was transported in a concreted state and kept wet with an alkaline gel (Carpenter 1987). Thus once the engine had been safely transported to the conservation laboratories in Fremantle, the deconcreting phase could begin.

The rate of corrosion of metals both in the marine environment and in treatment tanks is controlled by the combination of the anodic (metal oxidation) and cathodic (oxygen reduction) processes. Measuring the corrosion potential (E_{corr}) of the metal is a good way of monitoring how the rate of deterioration is changing according to the way in which the microenvironment is being changed. Since the E_{corr} varies according to the rates of metal oxidation and oxygen reduction, any changes in the value represent a measure of change in the environment of the artefact. The voltage measured refers to the difference in electrical potential of a reference electrode, such as a silver/silver chloride electrode (Ag/AgCl) and a working electrode such as platinum. By using a calibrated reference electrode it is possible to convert measured voltages onto the standard hydrogen scale, which is the standard for electrochemical and corrosion processes. In this report, all the voltages are reported relative to the standard

and Mike McCarthy (the team) working on the engine removing the mass of concrete, the engine was set up for conventional electrolysis treatment. This arrangement followed on from the initial use of an aluminium sacrificial anode being attached to the engine via the main copper exhaust steam pipe. A series of eight mild steel anodes were hung on insulated rubber and steel mounts from the side of the treatment tank which had the overall dimensions of 3m x 3.5m and 2m in total depth. During the early stages of the removal of the concrete it was apparent that the task was going to take several years of hard working conditions. There was very limited access to the lower sections of the engine assembly as it lay on bed of old rubber tyres and there was only just enough space to squeeze past the protruberances of the pipes and pumps. The high chloride content of the corroded mass was indicated by the removal of 2.47kg of chloride from the run off of water during an early deconcreting session of four days. The typical surface pH under the concrete, such as on the wiper shaft, was 4.53. Since nobody had experienced such a massive operation before, it was decided to treat the process like deconcreting a massive cannon and so keep the object wet by sprinklers during the mechanical removal of the marine encrustation.

One of the undeniable causes of physical damage to the corroded matrix of the cast iron was the method of hammering away with small dumpy hammers and a variety of chisels, bolsters and other home made devices. There was some significant damage to one of the trunks and to the main steam exhaust pipe in October 1986. When cast iron corrodes the pure iron phases are selectively corroded and then the pearlite, followed by cementite until there is only the inert graphite phase left behind which still retains the original profile of the object and incorporates all the inscriptions and ciphers. The inherent fragility of the engine can be guessed at when you consider the depth of corrosion (graphitisation) and the original wall thicknesses are typically 15mm. The main gasket flange on the forward trunk had a depth of graphitisation of 11mm or some 0.097mm/year, which is the same as the average marine iron corrosion rate of 0.1mm/year. The trunk itself was graphitised to a depth of 3.5mm or some 0.031mm/yr. Clearly there are many sections of the engine where corrosion has robbed it of any major solid metal and the apparently solid material is nothing but a mass of magnetite (Fe₃O₄) and graphite and some residual pearlite. Because of the effect of the geometry of the cast metal sections, the right angled

hydrogen electrode (NHE). The results from monitoring the E_{corr} of the main steam exhaust pipe during the initial treatment with sacrificial anodes are listed in Table 2.

Date	pH	E _{corr} volts vs NHE
May 1985	7.0	-0.450
May 1985	10.0	-0.532
June 1985	12.2	-0.562
July 1985	12.2	-0.667

Table 2. Effect of pH and anodes on E_{corr} for the main steam pipe during the first treatment stage.

The results of the combined pH and E_{corr} measurements are plotted on Pourbaix diagrams which are thermodynamic stability maps which show whether a metal is in an active, passive (slow rate), or immune region with regard to corrosion (Pourbaix 1974). It should be stressed that the corrosion potential is essentially a kinetic parameter, which reflects a non-equilibrium situation. The measurement of corrosion potentials is sufficiently reproducible to provide data sets between field seasons at the SS *Xanitho* (1872) site where the results are reproducible with an error of only ± 2 millivolts. The implications for site management and conservation of this reproducibility is that any measurement, which is different by three millivolts (3 mV), represents a change in condition. The depth of graphitisation of the cast iron fittings is a measure of the long-term corrosion rate that the object has experienced. Graphitisation is a term that describes the conversion of solid cast iron into a corroded matrix, which retains its original dimensions by preservation of the graphite (free carbon) phases in the degraded object. The linear relationship between E_{corr} and the logarithm of the annualised depth of graphitisation of the cast iron object means that a 3mV change would typically represent a 2.5% increase in the corrosion rate of the artefact (MacLeod 1995). A ten-fold increase or decrease in the corrosion rate would amount to a change of 320mV in the corrosion potential.

Deconcretion and Desalination

After four months of soaking in the treatment tank and several sessions of having a number of conservators

dissolution of calcite and aragonite, as a result of hydrolysis reactions) and methane, which came from the chemical reduction of carbon dioxide (Hunt 1979). The effectiveness of the concretion cover in slowing down the desalination is seen in the difference in the chloride concentration in the exposed and concreted iron. After two and a half years of treatment the mean value of the exposed cast and wrought iron sections was $0.033 \pm 0.02\%$ chloride while those surfaces freshly exposed had typical values of $0.40 \pm 0.08\%$.

One common problem for conservators using electrolysis for the first time is that very few literature reports include tables of typical values of anodic, cathodic and overall cell values, which can act as a guide to see how things are progressing. The data from 30 months of electrolysis of the *Kaniko* engine are listed in Table 3, that shows that roughly 50% of the power is lost through resistances in the circuit of the electrolysis cell. The difference between the cell voltage and the combined anodic and cathodic potentials is the voltage drop due to the solution and artefact resistance to the passage of the direct current. After the 30 months were up, the use of applied direct current from a voltage rectifier was changed over to a sacrificial anode in March 1988, because of concerns that the configuration of the tank may have been the cause of surface cracking of some of the edges. This was noticed on some of the flat plate sections of the steam pumps, which had been quite close to the anodes with less than 15cm separation between the cathodic and the anodic electrodes of the electrolysis cell. It was felt that the surface lifting and cracking might have been due to excessive hydrogen evolution. Just before the termination of the electrolysis treatment the average E_{corr} of the engine (measured at ten points) was -0.896 vs. NHE at pH of 12.50 for which the formal hydrogen evolution voltage is -0.740 volts.

Clearly the engine had been in a situation where hydrogen evolution would have been occurring but this had been the normal way of gentle electrolysis of more than a dozen iron cannon and the method had worked for them without any problems. The E_{corr} values of the engine during treatment with the aluminium anodes after electrolysis are listed in Table 4. Typical current output from the anode was of the order 17.5 amperes, which was distributed across the whole of the engine in the treatment tank. Some five months after the changedover to the sacrificial anode the tank was drained for further deconcreting work and it was noted that many edge sections had fallen off. The debris was

edges of the plates, flanges etc are corroded to a greater depth than the plane sections by a factor of approximately 1.4 times and this makes all the sharp edges very prone to loss.

During one of the cleaning operations it was noted that when a brass cock attached to the valve of the chest was opened, a white opaque liquid of saponified lallow drained away. This white solution had a chloride concentration of 4250 ppm, which was much higher than the plateaused solution value of 195 ppm. Clearly there were problems with the washing solutions gaining access to the many chambers and trapped spaces within the engine. Better methods of chloride removal from these restricted air spaces were needed.

In October the following year the engine was raised from the floor of the tank and placed on a steel frame which Geoff Kimpson had assembled inside the tank. Once this had been set up it was possible to safely work in the crawl space under the engine. The lower brass steam cocks were deconcreted and gas was let out prior to the liquid draining away with 22,000 ppm chloride from the portside cylinder in the air section. The chloride concentration of 10,250 ppm in the forward section clearly indicated that there was no movement of the solution within the cylinder. The packing glands around the trunk were still effective in keeping the wash solutions from penetrating the cylinder spaces. After two and a half years of work on the engine it still had chloride internal concentrations greater than the 18,650 ppm of normal seawater. By comparison, the starboard aft cylinder gave average solution concentrations of $3,803 \pm 858$ ppm chloride ions, which indicated that there had been some penetration of the treatment solution into this part of the engine. The forward drain cock of the same cylinder gave an average of $11,000 \pm 2,600$ ppm chloride, which showed that there was no solution exchange between the forward and rear sections of the cylinder.

When the drain cocks were opened there was a hissing sound: clearly the cylinders were both gas tight and solution tight. It is likely that the gas was similar to that evolved during the anaerobic corrosion of iron under concretions, where typical values of Eh and pH are -0.130 volts and pH 4.8, i.e. just below the hydrogen evolution potential for the same pH (MacLeod 1981). 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

Table 3. Voltage and current during electrolysis of the engine at pH 2.5 (±0.2).

Date	Cathode V	Anode V	Volts	Current, Amps
5/8/85	-0.487	+0.843	1.6	2.7
5/8/85	-0.525	+0.853	2.0	6
6/8/85	-0.575	+0.861	2.5	10.5
6/8/85	-0.747	+0.863	3.0	15
20/8/85	-0.948	+1.060	2.5	31.5
11/7/86	-0.936 ± 0.083	*	*	*
5/11/86	-0.721	+0.861	3.5	17.5
24/4/87	-0.896 ± 0.033	+0.933	3.5	15
16/3/88	-0.896 ± 0.057	+0.981	3.5	15

* Data not recorded

collected and it was recorded from which section of the engine it had come.

In September 1989 after some eighteen months of treatment with a sacrificial anode, the E_{corr} of the butterfly valve, the only section of the engine, which was readily accessible, was -0.083 at a pH of 10.7. At the time it was noted that the voltage was more than 80mV more positive than during electrolysis, but the cause and the implications of this were not realised. The same observations about elevated corrosion potentials of the steam pipe and other sections of the engine were noted six months later in March 1990 and again in December of that year. Despite the data indicating an underlying problem, the thoughts were that it was just a poor electrical contact with the corroded surface that was the cause of placing the object in the passive $\text{Fe}(\text{OH})_3$ zone of the Pourbaix diagram. In May of 1991 the corrosion potential was a bit more negative at -0.118 at a pH of 10.3 and the metal looked black and healthy so our concerns were somewhat allayed. More sodium hydroxide was added to the solution and the pH increased to 12.28 and the E_{corr} fell to -0.316 ± 0.008 volts.

In March 1992 with the aid of inmates from France, Brunei, Darussalam and Canada, we removed another 75 kg of concrete and the engine was out in the open for four days. In the new solution the pH was 12.45 and the E_{corr} was -0.450 which indicated that the metal was moving in the desired direction of lowered voltage. In July 1992 the E_{corr} values of ten sections of the engine were measured using a platinum electrode connected to long cables to the digital voltmeter above the tank. This appears to have caused some systematic

errors but it should be noted that the average E_{corr} of the engine components was 105mV anodic of the steel in the support frame. The less negative voltage is typical of the elevation of corrosion potentials by the carbon content of the cast iron.

In October of 1992 a further week of deconcreting saw the removal of the covers from the crankshaft bearings and the surface pH values ranged from 6.46-4.37 but in the crevice regions where there had been restricted access to solutions the pH was typically as low as 3.14! It seemed almost unbelievable that after seven and a half years of treatment there could be such residual acidity and chloride activity. These observations decided for us that the only option for saving the engine and its components was to completely disassemble the local structure. Unless the alkaline wash solutions could penetrate all the crevices then the object would be very susceptible to corrosion and collapse once it had gone on exhibition.

Thus it was in April 1993, eight years after recovery of the engine, the steam pipe, the crankshaft assembly and the cylinder blocks were separated from each other for the first time since the repair work carried out in Java in 1871. The difference in the chloride levels on concreted faces and previously exposed faces was dramatically seen with the butterfly valve which had only 0.4 ppm surface chloride on the exposed side, while the concrete interface still had levels of 4,800 ppm. Richard Garcia then commenced the slow task of gradually pulling the engine apart into its components and the cylinder blocks were stored in separate caustic tanks with typical pH values of 13.5 to ensure the passivation of the freshly exposed surfaces. It was

air, the surface pH fell to 3.5 in the areas of the cylinder wall that had received minimal solution washing. This problem existed despite regular flushing of the caustic solutions through the drain cocks in the bottom of the unit during the previous years of solution soaking and electrolysis. A direct measurement of the chloride concentration showed that this section of the cylinder had an activity of 15,456 ppm; clear evidence indeed of the need for the object to be further treated in alkaline solutions to remove the high level of chloride. At this stage after nine years of the project it fell as if we were just beginning again!

The Problem

After all the sections of the engine had been taken apart they were placed in a number of treatment tanks in 2% sodium hydroxide solutions with a pH of 13.2 ± 0.3 and soaked for ten months. During this time the cradles and anodes were made for the electrolysis of the trunks, the cylinder blocks and the crankshaft. The wrought iron sub-frame had been previously taken apart and is happily undergoing routine electrolysis treatment. When the current was turned on to the five treatment tanks the corrosion potentials were recorded at the surface of the objects and the voltage was adjusted to approximately 250mV more anodic than the hydrogen evolution potential for the given pH of the treatment tank. Inspecting the tanks 72 hours after the apparently successful initiation of the electrolysis treatment, it was a shattered conservator who came in and found that massive exfoliation had taken place. Virtually all the fine edges of the engine sections had peeled off or were hanging on by a small 'threads' of corroded metal. Examples of the problem can be seen in Figures 1-3. The conservator contacted the project leader, who was driven almost to despair by the turn of events. A critical review process ensued and the essence of the findings is revealed in the following discussion.

The Reasons

It is clear from the values of the E_{cor} that the measurement gave a reading that related to the voltage of the graphitised sections of the object and not the underlying metal. Similar problems have been noted with corroded cast iron ballast blocks from the wreck of HMS *Sirius* (1790) on Norfolk Island. After years of electrolysis, the blocks were rinsing in water to prepare them for a wax impregnation treatment. Six of the blocks gave E_{cor} readings of -0.197 ± 0.067 while two

Date	E_{cor} vs NHE	pH
22/9/89	-0.563	*
3/12/90	-0.056 poor connection	*
27/5/91	-0.316 ± 0.008	12.3
11/3/92	-0.450	12.5
9/7/92	-0.219 ± 0.051 suspect electrode	12.6
26/10/92	-0.486	11.3

* Data not recorded

Table 4. Voltage of main steam pipe with anodes after electrolysis.

clear that even the old exposed iron frame had chloride levels of 350 ppm while the freshly exposed sections had values of the order $1,965 \pm 155$ ppm, so the treatment was far from being over.

In order to assist the process of removing the very dense anaerobically formed rock-hard concrete from around the faces and within the very structure of the cylinders, one of them was soaked in a degreasing tank filled with diesel oil. It was an unfortunate coincidence that the 1.2 tonne weight of the cylinder unit found a defect in the tank, for only after some 24 hours of soaking the diesel level had dropped and the rest of the material had run into the ground! The cylinder was removed from the tank and stored dry under cover in the old conservation laboratories while the second cylinder was painstakingly disassembled. The trunk and piston gland was finally removed on Friday June 10th 1994 and this revealed a wealth of information about the state of the vessel and the subsequent changes in the site conditions. Corrosion lines on the inside of the forward wall of the cylinder block showed two zones which ran in different directions. Clearly water had entered the cylinder at the time of wrecking and the vessel lay to the port side at 31° and then after some time it settled onto the starboard side at 10° to the horizontal. Calculations of the volume of water contained in the forward section of the cylinder showed that the pressurisation was equal to a water depth of 3.5m which is typical of the depth before the vessel settled into the seabed.

The surface pH was measured across the length of the trunk and where it had been treated in the tank the values of 10.3 were found, and 7.0 was read at the surface which had been totally sealed against the walls of the cylinder. After the weekend of exposure to the

gave readings of -0.391 ± 0.055 volts vs. NHE in a pH of 10.39. Clearly only two of the ballast blocks had their graphitised layers in direct electrical contact with the core metal. The 194mV elevation of the E_{cor} value of the *Sirius* blocks meant that if similar problems were existing with the *SS Xanitho* engine components, then the volages had been adjusted to a point where hydrogen would be gradually evolved. The increasing hydrogen gas pressure caused the weakened graphitised materials to spall once the weak bond between the FeOOH at the metal-graphitised zone had been reduced to magnetite (Fe_3O_4). It is now clear that the elevated E_{cor} values of the engine meant that electrical contact between any residual metal in the artefact and the corroded surface zones had been lost. By looking back at when the changes in E_{cor} moved from the 'normal' negative values to more positive ones it appears that most of the damage took place within the space of eighteen months to three years of recovery. The timing was dependent on when the sections that had been exposed to the air with the removal of the concrete had seen internal corrosion at the interface between the graphitised layer and the underlying metal. The repeated spraying of the engine to keep it wet during deconcreting would have leached out the alkaline electrolyte and the good electrically conductive graphitised layer assisted the cathodic reduction of oxygen and so the iron corroded at the interface. The previous E_{cor} measurements that had shown the object to be in a FeOOH passive zone of corrosion were correct, but the iron(III) oxide was the growing problem, that electrically isolated the outer zone from the core of the residual metal.

Clearly one should not have sprayed the engine with water without the use of corrosion inhibitors in the water and the application of corrosion inhibitors directly to the exposed sections after deconcreting. During the months of dry storage of the separated engine components, a water dispersing agent should have been applied to the surface, in conjunction with an appropriate inhibitor, to minimise the damage to the delicate bond between the corroded and the uncorroded metal. The effectiveness of the water dispersants is demonstrated by the better performance of the cylinder block, which had been soaked in the diesel prior to its disassembly. Other problems of exfoliation had occurred because of the use of compressed air to circulate the water in the treatment tank. It was not realised until too late that this procedure was causing air to be trapped against the

underside of the cylinders and so the graphitised zone was corroded at the interface with the residual metal.

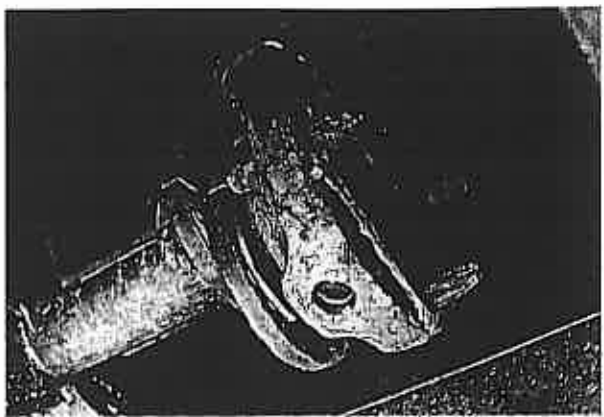


Figure 1. Exfoliation of aft end of crankshaft.



Figure 2. Exfoliation from one of the counterbalances on the crankshaft.

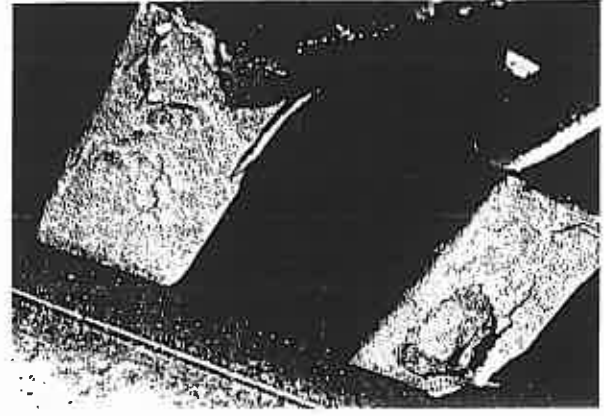


Figure 3. Partly delaminated graphitised zone on a crankshaft counterbalance.

penetrated the 4cm thick concrete to provide a good electrical connection which was confirmed by *in situ* resistance measurements. Insulated copper cables were brazed onto the 'C' clamps and the central steel core of the zinc anodes to provide electrical contact. The cost of two 28kg zinc anodes, six 'C' clamps and associated cable and crimps was \$250, which is very small when placed against the 'value' of the wreck material. With the outward diffusion of chloride ions occurring during cathodic protection, it may be possible to perform major parts of a conservation treatment before the object is raised. A summary of the history of the anodes on the stern section and how they have modified the corrosion environment is shown in Table 5.

From the values of the corrosion potentials and the pH, the anodes do exert a beneficial effect on the stem but there needs to be more regular inspection and maintenance since the site seems to consume the anodes within the space of three years. Operational constraints have prevented more frequent access to the site. The work done over the past decade on the stem section would have had lasting benefits. This is supported by the observations on materials treated on other wreck sites. Recent work on a concreted iron carronade from the *Sirius* (1790) has shown that chloride ions diffuse out from the dense concrete under the influence of the electrical current flowing from the sacrificial anode. In the space of three years, a total of 56kg of chloride ions were removed from the ordnance whilst it was still lying on the seabed. Monitoring on the seabed and in the laboratory after excavation showed that at least 80% of the chlorides had been removed from the carronade before

Tests on the drilled samples of the engine components will establish when the desalination process had been effected. Gentle electrolysis at voltages more anodic than the hydrogen evolution potential has been chosen as the only effective way in which the salts can be removed. The values chosen ensure that no hydrogen evolution takes place and that further exfoliation does not occur. Once the chloride has been extracted the degraded sections will be consolidated and the major pieces of exfoliant will be reattached. In cases where little substantial material remains, a composite mixture of the exfoliant and polyvinylbutyral will be used to re-establish the original profile of the cast iron sections. Laboratory tests have confirmed that this is an effective method of re-attaching the exfoliated sections and to infill areas of small losses (Tulloch 1998).

The Stern Section

The first zinc anodes were attached to the stern section of the *SS Xantho* in 1986 and were found to have been totally consumed by the time another inspection was done in 1989. The two 28kg zinc anodes were attached through six 'C' 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 (Kimpion & McCarthy 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

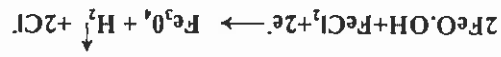
Future Prospects

The Engine

Table 5. Corrosion potentials and pH of stem section during *in situ* conservation treatment.

Date	Elapsed Time	Volts V _{Ag/AgCl}	pH	Observations
August 1983	initial inspection	-0.280	4.8	Pre-disturbance
April 1985	20 months	-0.419	6.6	Aluminium anode
May 1986	no anodes	-0.242		No protection
May 1986	with anode	-0.380		New zinc anodes
December 1988	19 months	-0.499	6.4	"
March 1992	39 months	-0.291	-	Exhausted anodes
March 1994	62 months	-0.289	6.7	Exhausted anodes
March 1994	-	-0.448	na	New anodes attached

excavation. This amounted to a total of 49.8kg of chloride ions or some 7.6% by weight (MacLeod 1996). Although the general environment of the stern section, as measured by the typical depth of graphitisation of the SS *Xantho* site of 0.12mm/year, is roughly half of that of the *Sirius* carronade, it is likely that about 100kg of chloride ions have already been removed from the corroded metal section. The cathodic protection pre-treatment means that the objects can be safely recovered and transported in a largely stabilised condition and can be prepared for exhibition in a relatively short space of time. During *in situ* treatment by sacrificial anodes, a possible equation that could describe one of the stabilising reactions is shown below:



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_3O_4). 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 (magnesian calcites) and the deposition of the iron carbonate siderite ($FeCO_3$). 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 corroded metal. The filamentous nature of the slag inclusions ($SiO_2 \cdot 2FeO$) 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. If the archaeological values of the stern section are regarded as paramount, then the *in situ* treatment of the stern section will allow it to remain in a stable condition on the seabed ready for the enjoyment of future generations.

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