

WESTERN AUSTRALIA — BAYLISS YOUTH LECTURE



SHIPWRECK CONSERVATION CHEMISTRY

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INTRODUCTION

What is a chemist doing at a museum?

I am not preserved in formalin, I still move, I am moderately flexible, so what is the story?

Why have a chemist in the museum if he is not an object of curiosity? The public in WA don't even pay to go along to museums, so what is the point of having a chemist there? Well, one of the things is that WA has an exceptional maritime heritage, there are approximately 1200 shipwrecks up and down the WA coast. The earliest one, the Tryal sank in 1622, so that is quite a long time ago. Most of our work of the museum in the maritime section has been centred on the excavation and subsequent treatment of the material of the Batavia which sank in 1629 and our work involves material recovered from shipwrecks which have been wrecked up until around about 1900 after which WA ceased to be a colony and it became part of the Commonwealth of Australia. So my time scale is from around about 1629 up to 1900. What I am going to talk about tonight is some of the work that we do at the Maritime Museum, the work that a chemist carries out in the stabilization of the objects which are brought up from the sea, most of which need some form of emergency treatment when they come up otherwise, they are going to fall apart. A very good example of this is cannonballs. If you take a nice 24 pound cannonball and start bowling it across the deck like Drake, you will knock off the coral that has grown around it for 350 years. The net result is that you have got a black sludgy mass in your hand, and it starts to get hot. Once the coral has come off, the cannonball starts corroding so quickly that they've been known to steam, and in some cases in the Mediterranean, get so hot that they have burnt through the decks of a wooden boat. Our job is to prevent the loss of the cannonball, for if you lose it you have lost its history. That is why chemists step in and prevent degradation.

The conservation laboratories of the Western Australian Museum are housed in the old Commissariat building which served as a convict built bond store in the 1850s. The building is down by the waterfront and was once the centre of colonial commerce but over the years it had become derelict. The Public Works Department restored the building which now has display galleries, the Maritime Archaeology Department and a reasonably well equipped conservation laboratory. One problem of working in a converted friable sandstone building is the walls keep fretting and dropping gritty dust onto one's desk when the door is slammed one floor below. We have our old laboratory at the other end of Fremantle where we treat massive objects such as cannons, anchors and sides of seventeenth century wooden ships.

Chemists must constantly be able to improvise and never are you more tested than when practising as an on-site conservator at a remote location where there is no fresh water or large storage vessels and all chemical supplies need to be ordered two months beforehand. On the Rowley Shoals 400 km west of Broome, heat-sealed black polyethylene sheets were used to convert large holes dug in the beach into caustic storage tanks.

A large part of my lecture will be concerned with material from the Batavia, our most infamous wreck, where many people were massacred after the ship was wrecked in 1629.

Why bother with chemists?

When cast iron objects are recovered from shipwrecks, the corroded metal retains all the markings of the foundry underneath a rock hard layer of coral. If the concretion is not carefully removed and the cannon placed in strong alkali solutions it will corrode at a greatly accelerated rate until all historic information has been spalled off the soft graphitized outer layers. In the days before chemists were employed as conservators some cannons were "neglected" and fell apart. Chemists are also needed to monitor the effectiveness of current stabilization procedures and to develop new techniques.

Similarly, if bronzes are not treated they will also corrode. People have been known to put away a nice collection of bronzes in a drawer and along comes a visiting ambassador, and they say, "Come and look at this". But when they open the cupboard all they end up with is a pile of green dust, which does not impress government ministers! As an electrochemist, I believe in water because I deal with the world's largest electrolyte solution, the ocean. It covers two thirds of the world's surface. The electrolyte is known to have certain inhomogeneities, it is slightly more salty in the tropics than down in Antarctica, but nevertheless it is a remarkably uniform material in which to carry out your experiments. By going down onto the wrecks ourselves we can get measurements which are the end results of experiments of up to 300-400 years duration. There is no way that you can duplicate in a laboratory the effects of 300 or 150 years of marine corrosion. The information that we have obtained on the way in which materials degrade has been used as a basis for advice to people such as the United States Nuclear Regulatory Commission who are most concerned about the way in which materials will degrade after hundreds of years on the seabed.

In Western Australia the waters are tropical to subtropical. We do not have situations like in the Great Lakes of North America where wooden ships sink, settle down on the bottom and remain intact. Tored worms love nothing more than a diet of good English oak, French oak, American oak or even Scott's pine, so what happens with a wooden shipwreck is that over the years it gets eaten right down to the waterline. Wood is only preserved along our coast if it has been buried either under a mound of rock, which may have been the ballast that the ship was carrying to keep it upright, or if it has been protected by coral or if it has been protected by the heavy silt like the *James Matthews* in Cockburn Sound.

With 100 tonnes of rock ballast to move from a shipwreck site simple physical chemistry is used to good effect. We go and load up "cray" baskets with the rocks and then go put air into an attached 80 litre drum until the basket has neutral buoyancy and then it's just swim, swim, push, push, drag, drag, drag, swim, mutter and go dump your rocks away from the wreck site, gradually exposing the hull timbers. If there is a massive object, such as a cannon, that requires shifting we will often attach a set of empty 200 litre fuel drums to the cannon. When filled with compressed air the volume of displaced sea water gives sufficient lift to enable the object to be towed back to the support camp. Compressed air also provides a useful aid to the underwater chemist when it is used as an "air lift". This simple device consists of a 15cm diameter PVC sewer pipe to which is

attached a supply of compressed air. As the bubbles lift the far end of the pipe they expand, as the water pressure decreases, and so provide the suction which draws up the loose sand and coral debris. After considerable work the site and the associated artefacts are laid bare and the whole area is mapped by using stereographic photography.

Modern doctors use various diagnostic tools to ascertain the health of a patient. Chemists can measure how "sick or otherwise healthy" their patients, i.e. our metal objects, are by sticking electrodes in them. That is one of the areas in which the W.A. Museum laboratories have been pioneers.

All the chemists have learnt to dive and work under water since there is no better way of getting to know your object than actually seeing it on the seabed. Recording on site parameters such as corrosion potentials (the voltage due to the corrosion cell composed of metal object and oxygen dissolved in the sea water) can be difficult on sites which are subject to strong surges. One may be just quietly drilling into an object to get a reading of its potential and all of a sudden you are not there, you are transported 4 or 5 metres away as another bit of surge comes through. A good grip is essential. Measurements of on site corrosion potentials are made using a platinum electrode and a silver/silver chloride/sea water reference electrode which is readily calibrated back on board the support vessel.

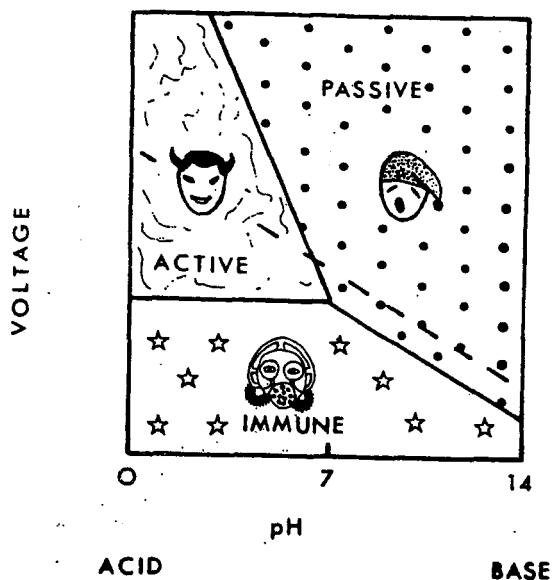


FIGURE 2: A schematic representation of a Pourbaix diagram for iron in water (dissolved species at $10^{-6}m$) showing the active, immune and passive regions.

There is a chemist called Pourbaix³ who developed a method to describe the state of metals in a very convenient form. If you know the voltage and the pH of the metal there are three regions in which metals can be classified, either "active" where you have active corrosion and the metal is slowly corroding away, or it can be passive state just sitting around not doing much at all, or it can be in a nice sterile, immune environment where no corrosion is occurring. For concreted iron artefacts the

following trends in corrosion potential and pH are generally observed.

As we drill in you find that the pH (from other measurements) drops and also the voltage drops until finally you are down in a region of active corrosion, underneath the coral, that lies below the line of stability of water. Underneath the coral there is quite a strongly reducing environment. One of the things that happens under the concretion is that you have got equilibrium between ferrous chloride and a mixture of ferrous chloride and ferrous hydroxide. As soon as you start excavating it, oxygen gets in and this material starts going off to green rust (I), which is a mixture of iron (II) and iron (III) basic chlorides. More oxygen goes in which oxidizes it up to our red-brown characteristic alpha, beta and gamma iron oxyhydroxides, which is the normal colour of rust, and Fe_3O_4 which is magnetite and which is black. The very easy way of finding out that it is magnetite is you get a little magnet and the black material will go and leap up onto bars of the permanent magnet.

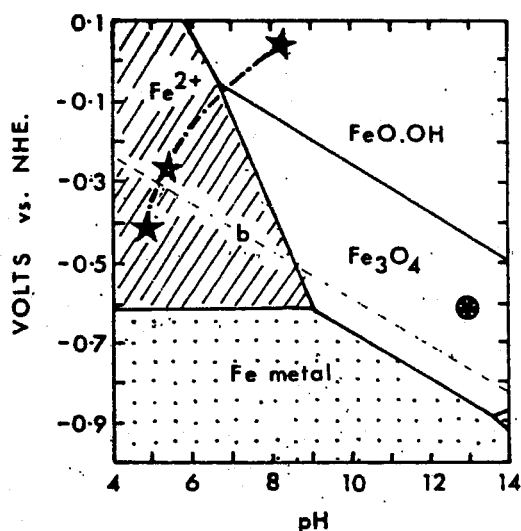


FIGURE 3: Pourbaix diagram for an iron cannon on the Rapid wreck site. The stars * show how the Eh and pH measurements change as the electrodes are brought from the seaward surface of the concretion up to the corroding metal surface. The other symbol shows the Eh and pH of the cannon after it had been placed in a caustic storage tank (it is in a passive state).

IRON CORROSION
under the concretion layer

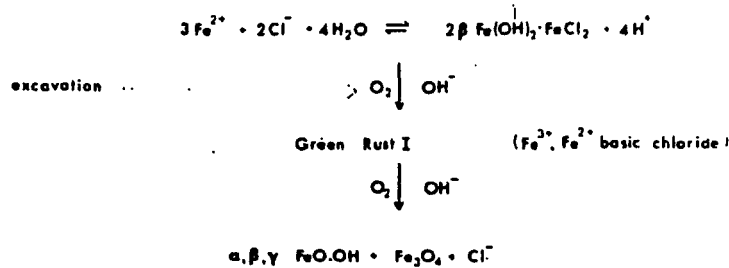


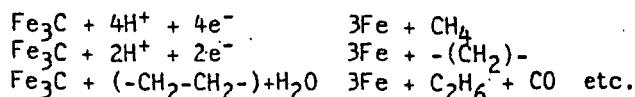
FIGURE 4: Schematic representation of equilibria involving iron before, during and after excavation - in the absence of conservation techniques.

When cast iron corrodes, it involves a series of phases, the names of which are ferrite, pearlite, cementite and graphite. Basically ferrite is pure iron, pearlite is a mixture of pure iron and iron carbide. Cementite is iron carbide, and graphite is carbon. So what happens, is that the more iron there is in the phase the faster it corrodes, so the pure iron "goes" first, then the pearlite, then the cementite to leave a residual graphite structure.

Consider the case of a load of small cannon balls from the Rapid which was found in a corroded container. All the balls were held in place by a matrix of magnetite and compounds such as the chloride containing $\beta\text{FeO.OH}_2$. During excavation the outer area of some of the balls was seen to have fallen off - such areas are mainly graphite and as such have little or no mechanical strength.

Cast iron, recovered from the sea as cannon or cannon balls, is often so soft you could shove your finger into the objects. Because of the fact that all the inscriptions on cannon are on the "outside" you have to be very, very careful in treating them so that you don't lose all that information which would otherwise help the archaeologist date that wreck.

Drilling into an iron concretion will often release gases, which were analysed in the following way. A fresh cannon ball was collected then ground up in a plastic bag full of nitrogen (so that air doesn't get to it) then put in a vacuum flask and distilled. It gave a most peculiar mixture which we call "Eau de cannon ball", which is really rather niffy. It is a combination of corrosion products and many other compounds, amongst which are a whole series of light weight hydrocarbons and acetylene. What happens is that the iron carbide reacts under the given experimental conditions with hydrogen ions to produce hydrocarbons, viz.



In a similar fashion, the strong reducing environment under the concretion (Eh -0.520, pH 4.8) will produce a range of hydrogenated sulfur and phosphorus containing compounds; such compounds help give corroded cast iron its characteristic odour.

I do not recommend making a whole mass of cast iron and burying it for a few hundred years as a way to solve the oil energy crisis, but one curious thing is that you often get massive coralline growths on cast iron with algae growing all over it. Lightweight hydrocabons have just recently been reported as acting as a sex stimulant for brown algae⁴ and now we think we know why it is that the brown algae love cast iron objects!

HOW DO WE TREAT LARGE OBJECTS LIKE CANNON?

After the concretion has been mechanically removed from the outer surface and the bore has been drilled free of coral, the cannon is placed on a cradle in a 0.5M NaOH solution. An iron electrode is hammered into the surface to get good electrical contact and then we make that the negative electrode of an electrolysis cell. Under the applied potential of approximately 6 volts the iron (III) corrosion products get reduced to a mixed iron (II)/iron (III) state, which gets converted to magnetite. Magnetite is much more dense than the iron (III) corrosion products and because it's more dense there are larger voids and so the chlorides diffuse out faster. Some critics say that since the Batavia was pulled up ten years ago, why aren't the lot of the Batavia cannons on display at the Maritime Museum? Well, we may be able to do miracles but even miracles take time! Don't forget those cannon were corroding for 350 years. The first of the batch of Batavia cannons are now just being finished after 7 years of electrolysis which has stabilised the cannons from the effects of 350 years of corrosion. I think we are on the winning side. The voltage is just sufficiently negative so that hydrogen is just starting to come off. The anode material is just expendable mild steel sheets; you obviously don't want to use your tank as the anode otherwise they would fall apart, quite dramatically. Some people in Britain thought, "Oh well, we will just adopt the W.A. Museum's procedure, we don't have the money for making these anodes we will just use the tank." One morning they came back and the tank was dry for it had big holes in it. A little embarrassing!

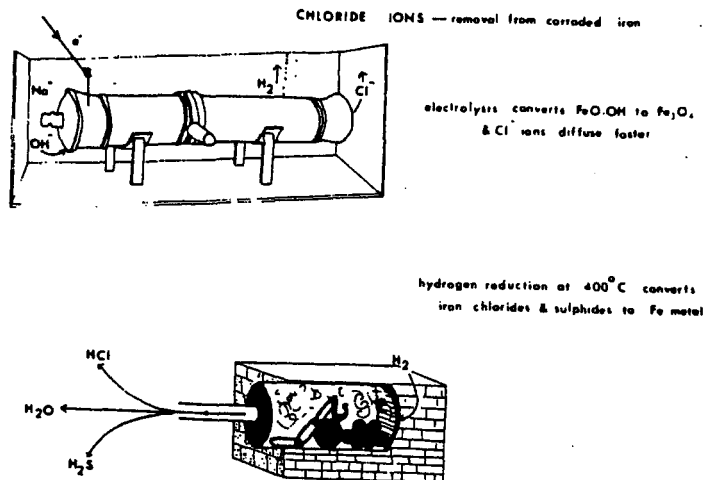


FIGURE 5: Diagram showing the main treatment methods for corroded iron artefacts.

We cannot make good electrical connections into highly corroded cast iron objects such as cannonballs. Cannonballs and other small items such as flat irons, rigging, hooks, chain plate etc. are treated in a hydrogen furnace. The air is replaced with nitrogen and the contents warmed to 80°C , to dry them out, in a hydrogen atmosphere. The temperature is gradually increased to 400°C for 24 hours. Although the equilibrium constant for the conversion of iron chlorides to iron is about 0.1 at 400°C we "force" the reaction along by having a continual flow of hydrogen through the furnace. The flow of hydrogen removes volatile materials such as HCl , H_2S and H_2O . After 24 hours in the furnace we cool them down and then wash out the last of the chlorides in a caustic soda solution. The latter process takes between six and ten months to finish.

What you have to be very careful with is that the treated cannonballs are a mixture of graphite and elemental iron. Because of its corroded state the treated iron is very finely divided and highly reactive; you have to get the cannonballs quickly into caustic solution to stop them corroding at a very rapid rate.

To finish the stabilization, after the chlorides have been washed out, we impregnate the cast iron objects in a bath of wax. When the wax solidifies it consolidates the outer graphite layers and provides a moisture and oxygen barrier which protects any residual metal.

TREATMENT METHODS FOR NON FERROUS MATERIALS: TEXTILES AND WOOD

Shipwrecks provide information not only about their cargoes but also give an insight into the lives and times of the crew. Some pieces of lace were recovered from the *Batavia* in a very sorry looking condition; the outline of the fabric was encrusted with red brown iron minerals. By using

iron complexing agents such as oxalic acid and ethylenediaminetetra acetic acid (EDTA), buffered to the optimum pH for stain removal without fibre damage, we were able to remove all the iron minerals. By removing the iron minerals the deleterious effects of their acid environment was effectively neutralized and the life of the textile prolonged indefinitely.

During excavations on the Batavia site a large section of the stern and port side was found in a natural depression in the reef. Coral debris and corroding iron had largely protected the wood from attack by marine worms. Although the wood is severely degraded and waterlogged, we can stabilize it by impregnation with a water soluble wax, polyethylene glycol. After 2 years in 60°C solution of gradually increasing wax concentration the objects are fully impregnated; we then dehumidify the timbers in a controlled environment for about 4 months. After dehumidification the timbers are brought into the Batavia gallery where the remains of the hull will be reconstructed.

The largest piece of timber we treated from the Batavia was a one tonne section of solid oak, called the fashion piece. To treat this artefact required a tank of 6.5m³ capacity and a total of 5.8 tonnes of polyethylene glycol 1500 a rather expensive "standard solution" which cost approximately \$8,000 to prepare. When it is realised that such massive structural timber came from a single oak tree it doesn't take much of a guess to explain why all the great forests of Europe disappeared during the seventeenth and eighteenth centuries.

SILVER:

Many of the Dutch East India men carried large quantities of silver bullion on their outward voyages since there was always a good exchange between hard cash and the prized cargoes of herbs, spices and ivory. Although the coins recovered from the Batavia, Vergulde Draeck and the Zuytdorp are of great numismatic interest they are often so corroded that their "value" is little more than that of scrap silver. Over the past five years several contemporary forgeries have been found on shipwreck sites such as the Batavia and the Rapid. A recent case from the Batavia was found as a hollowed out silver dollar - the sea had selectively corroded away the core and left a 'normal' coral encrusted outer layer behind. From an analysis of the corrosion products from inside the coin we calculated that a possible composition of the original material was 45.54% silver, 29.26% tin, 7.82% lead, 10.1% copper, 3.21% zinc, 2.3% iron, 0.93% iron, 0.66% bismuth and 0.16% nickel. Although the silver content appears to be high for a forgery such an alloy would have a melting point about 450°C lower than that of a genuine coin containing approximately 92.5% silver and 7.5% copper. The lower melting point would make the blank preparation a much easier casting process. The outer layers of the coin were typically high in silver and copper corrosion products but examination under a scanning electron microscope (SEM) showed the surface was microporous. The forged coin was treated by the standard chemical reduction treatment, using alkaline sodium dithionite⁷, and this showed up lettering which showed the coin to be from the Spanish Netherlands province of Gelderland during the reign of King Philip in 1568. All the mint marks were correct and it looked as though the coin would have passed detection were it not for 350 years of corrosion. By etching the blanks it would have been possible to enrich the surface layers in silver and copper so that, after stamping, the coins would look genuine.

After the *Batavia* was wrecked the sea water could have readily penetrated the etched outer layers to the debased metal core which was rich in tin. This would have established a corrosion cell between the inner and outer layers - a type of short circuited battery which operated until no more tin rich metal was left behind. Having lost the protection of the core, the silver rich outer layer would have corroded in the same way as a genuine coin⁸.

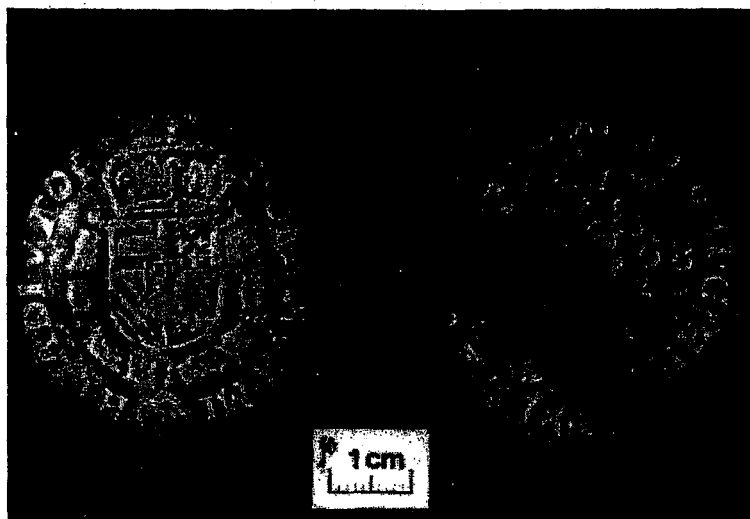


FIGURE 6: A forged Burgundian crown, dated 1568, from the *Batavia* after conservation treatment.

A coin from the *Rapid* was shown to be a forgery that had been made by silver soldering thin sterling silver tops and bottoms to central blanks which were made largely of copper. The forged blanks were then stamped at the Mexico mint in 1796. The forged coin bore the assayers mark and the assayers (chemists) were either unaware of the deception or were a party to it. Whatever the case, it was for them a dicey business since falsified analyses lead to removal of one hand and to castration⁹.

CERAMICS:

When ceramic materials such as jars, pots and plates are recovered from historic shipwrecks it is essential that they are given some desalination treatment. Salts gradually penetrate glazes and the underlying matrix so that after hundreds of years immersion they can account for up to 2% by weight of a saltglazed stoneware pot. If allowed to dry in an uncontrolled fashion the crystallizing salt solution will cause irreparable damage to the remaining glaze/surface of the artefact. Such problems are eliminated through wet storage in the field and by washing the objects in fresh water for six to twelve months back in the laboratory. Old glass bottles will often craze or exfoliate in paper-thin layers if desalination is not carried out. Once stabilized the task of sorting hundreds of thousands of ceramic shards is immense but our restoration department has very skilled staff. A total of 256 pieces were believed to have come from one pot on the *Vergulde Draeck* site and after reconstruction that was found to be correct, since 95% of the surface of the pot was able to be restored with those pieces. The missing bits may yet be found.

COPPER:

The problems of accelerated corrosion of copper were briefly mentioned in the introduction when a description was given to the conversion of solid metal to a pile of blue-green dust. Copper is a noble metal and normally corrodes in air to produce a largely protective cuprous oxide (Cu_2O) layer on its surface; the Cu_2O layer gives architectural bronzes that rich red brown colour. In the presence of high concentrations of chloride ions the whole chemistry of copper is changed¹⁰ and this is why we must wash copper based alloys recovered from shipwrecks. Instead of forming a stable oxide film the chlorides cause a cyclic corrosion reaction to occur (see figure 7) which leads to pitting and it can cause the eventual destruction of an artefact.

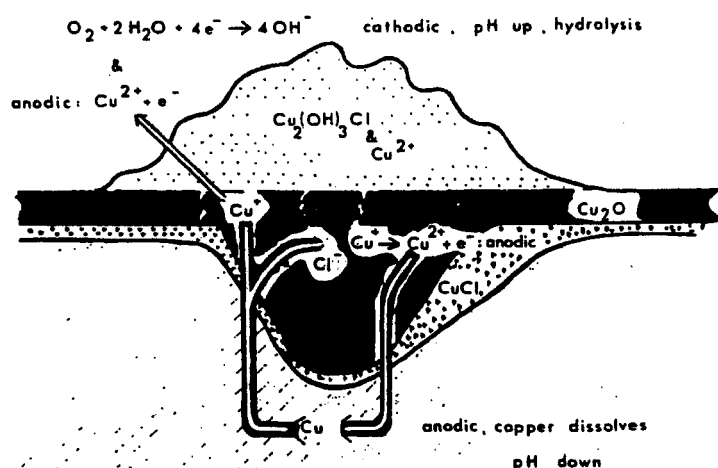


FIGURE 7: Schematic diagram for accelerated corrosion of copper (bronze disease) exacerbated by high chloride ion concentrations.

Chlorides can be removed by washing the artefacts in deionized water, in sodium sesquicarbonate or in alkaline dithionite solutions. The choice of method depends on the final patina that is required. Washing in deionized water does not change the surface colour of the object (its patina) but it is a slow process. Using a 1:1 mixture of sodium carbonate and bicarbonate (i.e. sodium sesquicarbonate) produces a solution of pH 10 (pKa for the $\text{HCO}_3^-/\text{CO}_3^{2-}$ equilibrium is 10) and such solutions increase the rate of removal of chloride ions since the higher pH increases the rate of hydrolysis of compounds such as CuCl . The sesquicarbonate washing will sometimes change the hue of the surface patina. The third scheme is to use alkaline dithionite solutions to treat the artefacts - since the dithionite reduces all copper corrosion products to copper metal, the patina is dramatically changed. The differences in the processes are shown

schematically in figure 8. In both deionized water and sesquicarbonate

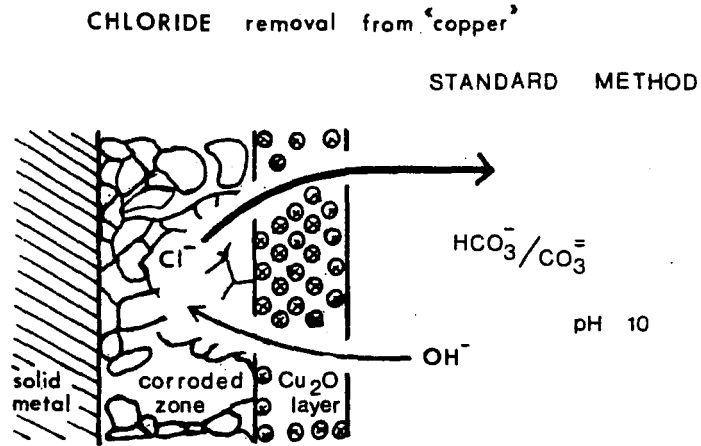


FIGURE 8a: Removal of chloride ions from corroded copper alloys in standard museum treatment conditions (pH 10 1% sodium sesquicarbonate).

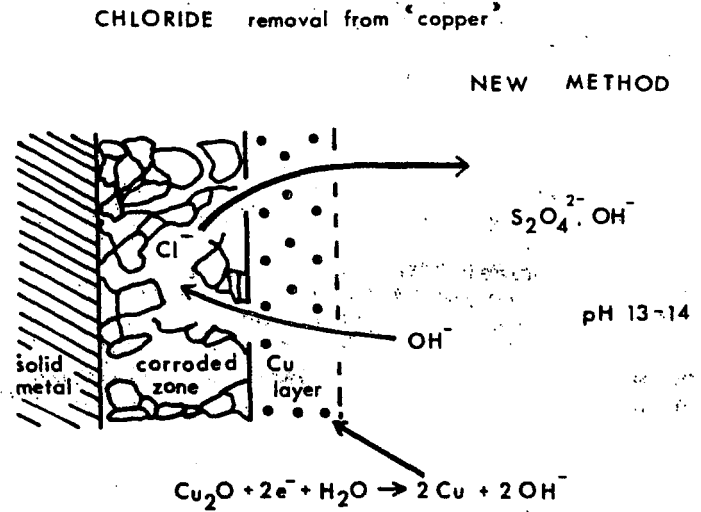


FIGURE 8b: Chloride removal from corroded copper alloys under reducing conditions (the alkaline dithionite method).

solutions the chlorides have to diffuse through the dense and adherent Cu_2O film whereas under the reducing conditions of the dithionite treatment the Cu_2O layer is destroyed and the chlorides simply diffuse away from the corroded metal. The difference in treatment times is most marked for the same object will take two years washing in deionized water, twelve months in 1 wt% sesquicarbonate and two weeks in a 5 wt% sodium dithionite/1 M NaOH solution.

FORENSIC SHIPWRECK CHEMISTRY

Apart from fulfilling the traditional role of a conservator of shipwreck artefacts, a chemist can often be of great use to the maritime archaeologist who is searching for clues about the origin of a particular wreck. A recently discovered wreck off the W.A. coast was a very interesting case because we found United States silver dollars on board, along with American copper coins and 19000 Spanish pieces of eight. The last date on any of the coins was 1809. At the time when the wreck was found nobody knew where it came from, or what it was doing here in Western Australia.

We knew that the wreck had probably gone down somewhere after 1810, since it takes a while for coins to get into circulation and, if it was American, before 1812 since America was at war - and its trading was severely curtailed.

We did not know why there were only 19000 dollars on the wreck since even in those days it wasn't enough to buy a full cargo. It was a bit much to be left over at the end of shopping, so we had to work out what was going on.

Amongst artefacts recovered from the 0.5m sediment layer on the wreck site were some barnacles (*megabalanus tintinabulum tintinabulum*) which had been attached to part of the bowsprit rigging. When barnacles are sectioned growth rings are readily apparent and the composition of this skeletal material is both temperature and salinity dependent. If the salinity of a site is known the ratios of the O^{18} to O^{16} isotope in the calcite (CaCO_3) layers will reflect the ambient temperature. The results of the isotope analyses are shown in figure 9 where the initial temperature begins at 25°C, drops to a minimum of 21.5° and the final reading was 27.5°C.

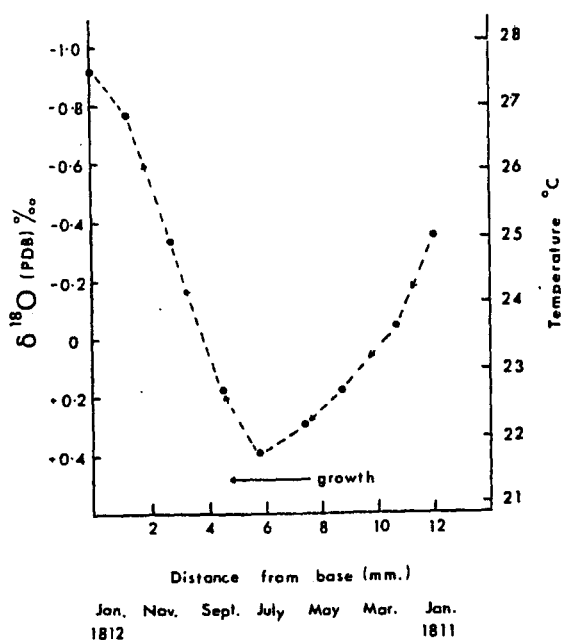


FIGURE 9: Plot of sea water temperatures on the Rapid wreck site from c. January 1811 to January 1812, deduced from the variations in ^{18}O found in the barnacles recovered from the site. ^{18}O per ml is defined as $[(^{18}\text{O}/^{16}\text{O}) \text{ sample}/(^{18}\text{O}/^{16}\text{O}) \text{ standard} - 1] \times 1000$. PDB is an international standard.

Since the growth rate of this species of barnacle and the type of micro-environment it prefers is known it is possible to interpret the data as follows. The barnacles began to grow on the rigging when the ship foundered and they grew for between twelve and fourteen months before the ship broke up. Since the maximum temperature was below the 29°C of equatorial waters which the barnacles would have experienced on a return voyage from China, it showed the ship was wrecked on its outward journey¹¹. Later research showed that the vessel was the American ship Rapid which had struck the reef on Monday night the 7th of January 1811. The Captain realising that the ship was stuck, hard and fast, was concerned over the 280,000 silver dollars on board (in terms of modern buying power, that was about 45 million dollars). He burnt his ship to the waterline to stop other people seeing the wreck, and then the crew manned the boats and rowed, sailed all the way up to Indonesia where they picked up another ship and went back home and later on arranged the salvage of the bulk of the money.

Since the barnacles have provided sea water temperatures for the period 1811 to 1812 and we have current data, estimates can be made as to the mean temperature over the past 170 years. With a mean value of 24.5°C the Rapid wreck site is a good "controlled" environment for long term corrosion experiments.

Apart from giving numismatic information and insights into criminal activities silver coins also record changes in the microenvironment of a shipwreck. When sterling silver coins corrode in aerobic sea water the major silver corrosion product is silver chloride (chlorargyrite) silver sulfides predominate in anaerobic or in heavily polluted environments. During electron microprobe analysis of some of the coins from the **Rapid** it was found that there was a banded formation with alternate layers of silver chloride and silver sulfide (see fig. 10).

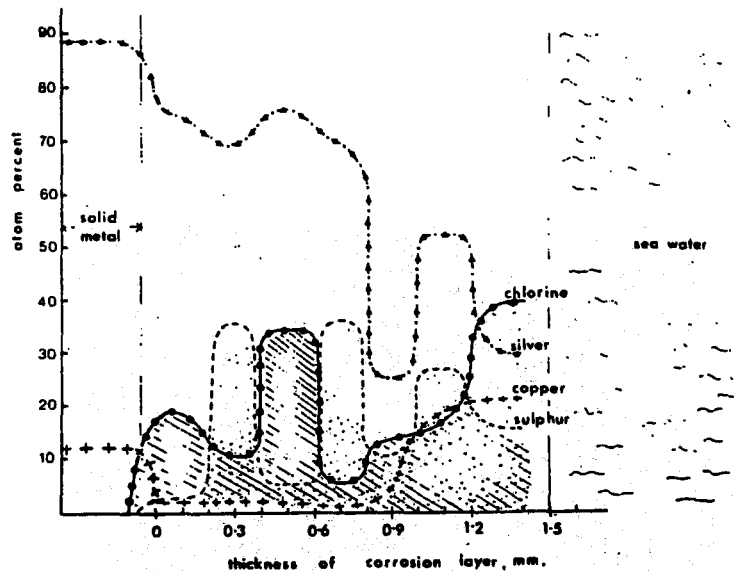


FIGURE 10: Plot of the distribution of silver, copper, chlorine and sulfur in the corrosion product layers found on a silver dollar recovered from the wreck of the **Rapid**.

The distribution of the elements shows that the more reactive copper is generally selectively corroded from the coin and that it tends to be precipitated at the coin-sea water interface. A possible explanation of the different "bands" is that after the ship was wrecked the coins corroded in aerobic (oxygenated) sea water and formed a coating of silver chloride. As the wreck settled some of the coins became buried in the sand where sulfate reducing bacteria provided a sulfide ion source to precipitate silver as silver sulfides. The coin was subsequently exposed and reburied etc. The site is sheltered behind an offshore reef and only major activities such as cyclones could create such significant changes on the sea floor. Meteorological records show that two intense cyclones crossed over the wreck site in the past eighty years so it's not unreasonable to assume that over the past 170 years between three and four such disturbances have occurred¹².

The identification of a shipwreck site is normally dependent on a series of observations which, when considered together, lead to a firm conclusion. The individual parameters can easily have an alternative interpretation. The wreck of the Rowley Shoals is believed to be that of the **Lively**, a French built vessel that was captured by the English and refitted (resheathed) as a whaler. The size of her armaments, the timber fragments and her construction are all consistent with the tentative identification. Amongst the artefacts recovered from the wreck were hundreds of "copper"

sheathing tacks and a few fittings associated with the ship's rudder. Some of the sheathing tacks were sectioned and analysed using the SEM and a metallographic microscope. This examination showed that there were two distinct types of tacks; the first was largely pure copper which had been hot worked and the second had a cast structure. Wet chemical analysis showed that the bronze tacks had different ratios of the trace metals of arsenic, antimony and silver to those found in the rudder fittings. The ratios of certain trace metals can be sometimes used as a guide to the provenance of artefacts since different ores give different ratios but the ratios can change during smelting and casting operations. Considered on their own these observations prove nothing, but when viewed in the light of the other data on the wreck it is not unreasonable to suggest that the "bronze" tacks came from a different source to the rudder fittings. The two different types of tacks may have come from the original sheathing and the refitted areas of the *Lively*¹³.

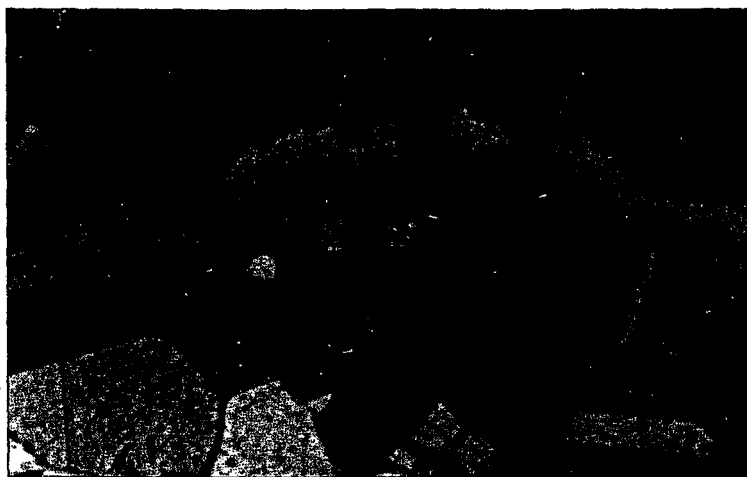


FIGURE 11a: Section of sheathing tack from the Rowley Shoals wreck. This tack has been hot worked and is made of 99.5% copper. Full width 140 μ m.



FIGURE 11b: Scanning electron micrograph of a corroded bronze sheathing nail from the Rowley Shoals wreck. Solid metal is in the lower left hand corner with corroded material above it showing residual dendritic (cast) structure. The material in the upper right corner is copper impregnated marine organisms. Full width 2.5mm.

GAS LAWS - A SPECIAL APPLICATION

When working under water, museum chemists will normally use a "hookah" system where a supply of compressed air is delivered by a hose. Ordinary scuba tanks do not last long enough if you are doing heavy physical work. The only thing that causes consternation is when you are right in the middle of doing something and you go and take a breath and nothing happens. It is then you have to remember to keep calm. All that has happened, (there is nothing wrong!) is that they have run out of petrol in the air compressor on the boat, so it has to be filled up. You just have to lie there doggo. If one person decides that they are going to panic they take the little air that you are getting and so you then have to quietly take the demand valve out of your mouth, you leave your mouth open and slowly swim to the surface on an empty breath. The reason why you have to do that becomes obvious if you look at the Gas Laws. Working under ten metres of water the total pressure is two atmospheres and your lungs have the same capacity as at the surface. If you go up to the surface with a closed mouth the gas wants to expand to twice the volume and since your lungs do not expand that much something has got to give. That is where divers can get into trouble with an air embolism, a little bubble of air can burst through your lungs and go into your brain. If that happens it can lead to death within 30 seconds. So chemists have to keep calm and remember the Gas Laws!

Another good example of the use of the Gas Laws is in the use of lifting bags to raise objects such as cannon or anchors from the sea bed. The Pandora site off the north Queensland coast lies in 30m of water where the total pressure is 4 atmospheres. If a large bag is partly filled with air the volume of the bag will increase as the cannon begins to ascend since the pressure decreases by one atmosphere per ten metres of sea water. As the bag expands, the volume of displaced water and hence the lifting power increases and the cannon begins to ascend at an increasing rate. Unless some air is released from the balloon the cannon will rocket to the surface where the bag will suddenly deflate and then the cannon will fall back to the bottom - ouch!

CONCLUSION

I hope that you can now see why chemistry is so important to the preservation of our maritime heritage. Every branch of chemistry is used to solve problems that arise during the analysis, treatment and stabilization of organic and inorganic materials that are brought up from shipwrecks. Not only do chemists in the shipwreck conservation business get to work in exotic locations but also they have the chance to make a lasting impression on the future, for without their work much of our heritage would be lost for all time. The work is demanding, frustrating at times, but above all it is fun!

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After completing his Ph.D at the University of Melbourne under Prof. Tom O'Donnell, Ian switched from polarography of metal fluorides in anhydrous hydrogen fluoride to organophosphorus chemistry at the University of Glasgow. Under the guidance of Prof. David Sharp he used the techniques he had acquired with handling highly reactive, moisture and oxygen sensitive compounds to develop a range of phosphino and phosphinothioethanes and to check out their catalytic properties in conjunction with platinum compounds. Nearly three years were spent under the late Prof. Jim Parker at Murdoch University studying the electrochemical behaviour of copper in aqueous-organic solvent mixtures. This work had direct bearing on optimising conditions for copper extraction from parent ores.

Six years ago he began work with Dr Neil North at the Western Australian Museum on the corrosion of non-ferrous metals on shipwrecks off the Western Australian coast, and in that time has developed several new treatments for stabilizing corroded metal objects ranging from pewter chamber pots to golden angels.