

OBSERVATIONS ON THE EXTRACTION OF IRON AND CHLORIDE FROM COMPOSITE MATERIALS

Ian D. MacLeod^{1*}, Paul Mardikian² and Vicki L. Richards¹

¹ Department of Materials Conservation, Western Australian Museum, Fremantle, Western Australia 6160, Australia

² ARCHEOLYSE, Underwater Archaeological Conservation Laboratory
1 Place de l'Aubarede 06110 Le Cannet, France

ABSTRACT

A series of experiments were performed on corroded cast and wrought iron recovered from a marine environment and on iron-impregnated waterlogged oak wood from the *Day Dawn* (1886). The results of the various tests showed that the most effective extraction of chlorides from corroded iron was found with the use of 2%(w/v) ammonium citrate solutions in association with 5%(w/v) PEG 400 at neutral pH. A comparison of this data with traditional washing treatments, such as 2%(w/v) sodium hydroxide solutions for corroded iron, indicates that the change to strongly alkaline solutions does not markedly improve the overall extraction efficiency of the treatment. Although there were obvious treatment time and chloride extraction rate advantages in using electrolysis in alkaline media the effect of cathodic protection on true composite artefacts recovered from wreck sites was not investigated.

The effect of dithionite and citrate at neutral pH on the surface of the iron-impregnated oak wood was examined. Fourier transform-infrared (FT-IR) spectroscopic examination of microtomed sections of this experimental wood showed no adsorption of these chemicals. The treatment methods mentioned above have not been applied to composite artefacts to date but we believe that these procedures have great potential in the area of pretreatment and desalination/consolidation of waterlogged wood/iron composite artefacts.

INTRODUCTION

Conservators are constantly plagued with the problems encountered when stabilising composite wood and metal artefacts. The problems are typified by the treatment of composite iron and wooden objects. The iron(III) corrosion products are known to catalyse the degradation of cellulose¹ and the corrosion products are inherently acidic as a consequence of the hydrolysis of the ferric ions. Moisture retention of archaeological wood is also a major problem since iron metal will actively corrode at relative humidities above 20%². Although physical separation can often overcome the traditional problems of treating intimate mixtures of iron and waterlogged wood, this option is becoming increasingly unpopular since such activities are viewed as an inherent violation of the integrity of the artefact.

Previous studies by the authors³ had shown that the optimum concentration of PEG for extracting iron corrosion products and chloride ions from both iron-impregnated concretions was in the range of 5-10% (w/v) PEG 1500. Subsequent experiments studying the effect

* Author to whom correspondence should be addressed.

of a variety of complexing agents on the removal of iron corrosion products from iron-impregnated waterlogged archaeological timbers' have shown that, in neutral solutions, the best result was obtained with a combination of citrate, as the iron(III) complexing agent and a dithionite pre-treatment to reduce and solubilise surface corrosion products, such as FeO.OH.

In order to develop these results into a possible treatment method for wood-iron composite materials, a series of experiments were conducted using deionised water, 5%(w/v) PEG 400, 2%(w/v) ammonium citrate with 5%(w/v) PEG 400, 2%(w/v) sodium hydroxide and electrolysis in 2%(w/v) ammonium citrate as desalination solutions for corroded wrought and cast iron recovered from marine environments. The effectiveness of these solutions on chloride extraction and metal corrosion behaviour were assessed. Additionally, the effect of citrate and dithionite solutions on the surface of the iron-impregnated waterlogged wood were evaluated after drying.

EXPERIMENTAL

Chloride Removal from Iron

The remains of the *Long Jetty* situated in *Bather's Bay*, Fremantle was built in the 1890's and the corroded wrought iron used in these experiments was obtained from areas adjacent to the jetty remains. The cast iron samples were obtained from the *Tamerlane*, which appears to be the remains of a hulk that sank in 1918 at the North Mole, Fremantle. The metals were covered with a layer of marine concretion⁵ which serves to concentrate the corrosion products and their hydrolysates in the area adjacent to the metal. The complex mixture of marine organisms and corrosion products acts like a semi-permeable membrane that separates the two halves of the corrosion cell and results in a significant increase in chlorinity and acidity underneath the concretion.

The concretion was mechanically removed from the wrought iron sample and a section of the 21±2 mm diameter wrought iron bar was cut into 41±5 mm lengths. The metal surface was extensively corroded and showed all the characteristic signs of preferential corrosion along the lines of working⁶. One sample of wrought iron was placed in each of the following solutions; distilled water, 2% (w/v) ammonium citrate 2% (w/v) sodium hydroxide, 5% (w/v) PEG 400 and 5% PEG 400/2% ammonium citrate. The final sample was electrolysed in 2% (w/v) ammonium citrate.

Cast iron sections were cut using a dental drill so as to retain the concretion on one surface of the coupons which were approximately 40 mm long, 30 mm wide and 10 mm thick. One cast iron section was placed in each of the following solutions; distilled water, 2% (w/v) sodium hydroxide and a mixture of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400.

The total solution volumes were one litre. The solutions were sampled at various intervals over a total period of 52 days to obtain chloride analyses. Chloride ion concentrations in these desalination solutions were determined using a Jenway Chloride Meter. The electrolysis experiment was carried out using a Johnson Matthey (240V.50Hz.75VA) DC voltage source and stainless steel mesh anodes, at a voltage of 2.5

volts. The cathodic potential was -0.888 volt vs Ag/AgCl and hydrogen evolution caused convective stirring. Apart from the electrolysis experiment none of the solutions were stirred.

Three low carbon mild steel coupons (60 x 25 x 2mm) had previously corroded over a six year period in the conservation laboratory. The surfaces possessed a moderate coating of rust before the surfaces were cleaned using 1200 grit wet and dry carborundum paper. Prior to use, the coupons were degreased in acetone. One side of each coupon was half masked with electrical tape to assist with the visual interpretation of the corrosion effects of each treatment. One coupon was then immersed in each of the following treatment solutions; distilled water, 2% (w/v) ammonium citrate and electrolysis in 2% (w/v) ammonium citrate for 13 days. The electrolysis was performed as above but at a cathodic potential of -0.850 volts versus Ag/AgCl or -0.650 volts versus the normal hydrogen electrode (NHE).

Concentrations of potassium, sodium, calcium and magnesium ions in the treatment solutions were determined by direct sampling using a Varian AA4 spectrophotometer with an air/acetylene flame. All chemicals were laboratory reagent grade.

Iron Extraction from Wood

A sample of dry, heavily iron stained wood of unknown origin was placed in a phial containing 2% (w/v) ammonium citrate solution. The solution was monitored and changed every two days for one week and once a week for the next two weeks. The wood was removed and replaced in a 2% (w/v) ammonium citrate and 5% (w/v) sodium dithionite solution mixture for a further 7 days. The wood was removed after this time, rinsed in distilled water for two weeks before air drying to reveal a weight loss of 1.118 grams or 17.8 wt%.

A sample of iron-impregnated oak timber was recovered from the wreck of the *Day Dawn* (1886) which was an American vessel, built in 1851, that ended its days as a coal hulk in Careening Bay, Cockburn Sound, Fremantle. One small section of the wood was placed in a 5% (w/v) sodium dithionite solution and another section in a solution of 2% (w/v) ammonium citrate. The sections were immersed in these solutions for 200 hours. The wood was then washed with deionised water and air dried. A 5 μ m top slice and five other 5 μ m slices at depths of every 200 μ m were microtomed from each sample and examined by a Digilab FTS-80 Fourier transform - infrared (FTIR) spectrometer using a diamond anvil cell accessory. All chemicals were laboratory reagent grade.

CHLORIDE EXTRACTION FROM CORRODED WROUGHT IRON

The extraction of chloride from the wrought iron in the various desalination solutions was monitored over approximately two months and the data was plotted to facilitate the interpretation of the kinetics. Five of the six treatment solutions followed normal diffusion controlled kinetics which gave linear chloride release when the concentration was plotted against the square root of the treatment time. The solution mixture of 5% (w/v) PEG 400 and 2% (w/v) ammonium citrate did not follow $t^{1/2}$, linear or pseudo first-order (i.e. $\log_{10}t$) kinetics and so the chloride release rate of wrought iron in this

particular treatment solution cannot be evaluated in the same way as the other samples. Further experimental work is needed to clarify if analytical problems were the cause of the data from this solution not giving good correlations with the expected pattern of diffusion controlled kinetics for the extraction of chlorides. The results are summarised in table 1 and diagrammatically represented in figure 1.

Table 1 : Chloride extraction from corroded wrought iron.

Results	H ₂ O	5% PEG 400	2% citrate	5% PEG 400 & 2% citrate	2% NaOH	Electrolysis 2% citrate
Wt % chloride	0.125	0.49	0.82	1.04	1.16	2.64
Wt % Cl at 26 days	0.105	0.41	0.74	0.97	0.90	2.57
Normalised release rate $\text{ng.cm}^{-2}.\text{hr}^{-1}$.	0.07	0.10	0.76	*	0.85	2.8

* The data obtained from the chloride ion extraction experiment in 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 did not follow diffusion controlled kinetics.

The tabulated data shows that the 5% (w/v) PEG 400 solution and the 2% (w/v) ammonium citrate solution were 4 and 6.5 times more effective at removing chloride ions than distilled water, respectively. However the combination of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 was even more effective. The total amount of chloride ions removed in the combined solution was 1.04 wt%, 8.5 times more efficient than in distilled water. Previous work has confirmed that low concentrations of polyethylene glycols can act as complexing agents for FeCl₂ and other iron corrosion products and this phenomenon can be rationalised in terms of changes in the colligative properties, such as viscosity, of the PEG-water solvent system³. Similarly, earlier experiments have shown that the enhanced performance of the neutral citrate solutions is due to the formation of an iron (III) hydroxy citrate complex which will dissolve Fe(OH)₃ at a pH of approximately 6.2⁴. Hence the synergistic effect of citrate and PEG on chloride extraction is not surprising. Notably, the total amount of chloride ions extracted by the combined solution was less than the sum of the totals released in the 5% (w/v) PEG 400 and the 2% (w/v) ammonium citrate solutions. This result is not unexpected as there will be competition on the surface of the corroded metal between the adsorption of the PEG and the citrate ions.

Similarly, it can be seen from the kinetic data shown in Table 1, that at a time of 26 days ($t^1 = 24.98$) the combined 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 solution had removed 0.97 wt% chloride while the 2% (w/v) sodium hydroxide solution had extracted 0.9 wt%. It should be noted that the latter solution had not plateaued at the time of comparison and the other treatment solutions had reached a relatively constant value of chloride ion concentration. Given that the storage of composite iron and wood materials in 2% (w/v) sodium hydroxide is far from desirable due to alkaline degradation of the cellulose structure in the wood, the neutral pH provided by the combined 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 solution appears to be a good storage medium.

Where there remains sufficient solid iron in the composite artefact there always exists the possibility of performing electrolysis of the metal while it is sandwiched between the wooden sections of the artefact. The data shown in table 1 and in figure 1 indicates that the electrolysis of the wrought iron in the 2% (w/v) ammonium citrate solution will enhance the chloride release rate by a factor of approximately 3.7 times compared to the extraction rate observed in the same solution without electrolysis. This increase is typical of the effects of electrolysis on the rates of chloride ion extraction from corroded iron^{8,9}.

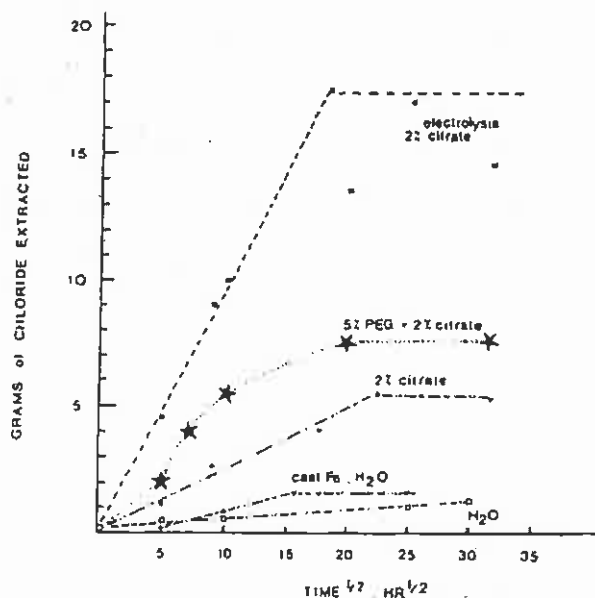


Figure 1 : Plot of the weight of chloride ions extracted from corroded wrought iron as a function the square root of treatment time, for some of the wash solutions.

The fall in chloride ion concentration in the latter part of the electrolysis treatment is due to the incorporation of chloride ions in the corrosion products on the anodes. Similar type of behaviour has been observed by the authors in the treatment of archaeological iron. It should be noted that the cathodic potentials used in this experiment were in excess of the hydrogen evolution potential. If these electrolysis parameters were used with an authentic wood/iron composite artefact, the confined space of the wood/metal interface would tend to become alkaline, causing deterioration of the organic component. Hence, if electrolysis is used, the voltage must be carefully controlled if such problems are to be avoided.

In order to assess the effect of 2% (w/v) ammonium citrate solutions on the corrosion of wrought iron, a set of previously corroded, slightly pitted, mild steel coupons were monitored for a period of 13 days. Corrosion of the coupons in distilled water and a 2% (w/v) ammonium citrate solution were compared with electrolysis of a coupon in 2% (w/v) ammonium citrate. The voltage (-0.850 vs Ag/AgCl) was chosen to ensure that the iron was in the immune region of the iron

Pourbaix diagram at pH 7.0. Examination of the surfaces was limited to optical microscopy under X40 magnification which was sufficient to show increased surface corrosion for the coupon in distilled water. The 2% ammonium citrate solution stripped the corrosion products from the coupon surface and the corrosion pits but there was a small amount of overall corrosion which produced a mildly etched surface. By way of contrast, the coupon electrolysed in the 2% (w/v) ammonium citrate was free of any surface attack.

Interpretation of the results obtained from these initial desalination experiments of marine wrought iron suggests that the most appropriate storage solution for wood/iron composite artefacts may be an aqueous mixture of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400. Not only will the corrosion promoting chloride ions be extracted from the iron at a reasonable rate but the PEG will begin to stabilise the waterlogged wood. However, it should be noted that it is necessary to add some form of corrosion inhibitor such as oxalate or tannate to the solutions to minimise further corrosion of the metal⁴.

Electrolysis in 2% (w/v) ammonium citrate proved to be the most effective method for extracting chloride ions but further work is needed to establish the most suitable current densities and voltages which can be safely used when the iron is in close physical contact with degraded, waterlogged wood. Simulation experiments with artificial composites of naturally corroded iron and waterlogged iron-impregnated wood are needed before this treatment can be fully assessed.

CHLORIDE EXTRACTION FROM CORRODED CAST IRON

Since many composite materials contain cast iron components, such as cokes in wooden pulleys with wrought iron bands, it was necessary to establish if cast and wrought iron behaved in a similar fashion. Having established the efficacy of treating corroded wrought iron in a solution mixture of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400, it was decided to make a comparison of chloride release from cast iron in distilled water, 2% (w/v) sodium hydroxide and the combined solution at neutral pH. Chloride release in the distilled water and the 2% (w/v) sodium hydroxide solution followed normal diffusion controlled kinetics and the same kinetic behaviour of the combined 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 solution was observed in both cast and wrought iron. The results are summarised in table 2 and shown diagrammatically in figure 2.

Table 2 : Chloride ion extraction from corroded cast iron.

Results	H ₂ O	2% NaOH	5% PEG 400 & 2% ammonium citrate
Wt % chloride removed	0.65	3.89	3.2
Wt % Cl removed at 26 days	0.646	3.50	3.2
Normalised release rate mg.cm ⁻² .hr ⁻¹	0.35	3.37	*

*The data obtained from the chloride ion extraction experiment in 2% ammonium citrate & 5% PEG 400 did not follow diffusion controlled kinetics.

Comparison of the diffusion controlled release rates of chloride ion extraction between the distilled water and the 2% (w/v) sodium hydroxide solutions showed that the caustic solution extracted chlorides 9.6 times faster than distilled water. This result is very similar to the value of 12.1 for the same media with wrought iron.

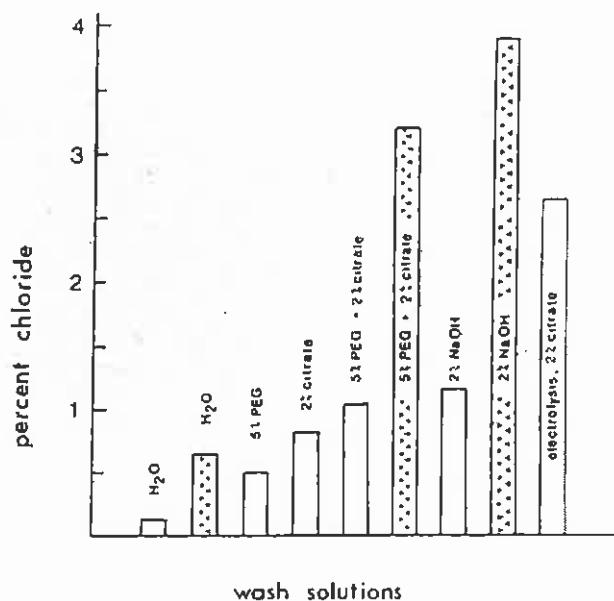


Figure 2 : Plot of the weight percent of chloride ions extracted from wrought and cast iron in various treatment solutions. (Hatched areas for cast iron.)

The tabulated data also shows that 2% (w/v) sodium hydroxide solution and the combined solution of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 are approximately six and five times more effective at extracting chloride ions from corroded cast iron than distilled water, respectively. It is possible to make a similar comparison of the amount of chloride extracted after 26 days of treatment for the cast as for the wrought iron. Again, inspection of the data in table 2 indicates that the combined solution of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 had extracted 91% of the total chloride released in the 2% NaOH solution over this period of time. Hence, the data demonstrates that for corroded cast iron/wood composite artefacts the optimum storage environment would appear to be a solution mixture of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 at neutral pH, provided an appropriate corrosion inhibitor, such as oxalate or tannic acid is present in the same solution⁴.

A comparison of the effectiveness of the various treatment solutions is shown in figure 2 which displays the weight percent chloride extracted from the cast and wrought iron at the end of the 52 day time period for these experiments. The amount of chloride ions removed from the cast iron is significantly higher than the concentration of chlorides released from the wrought iron but this is probably a reflection of the differences in metallographic structure. The combination of ferrite, pearlite, cementite and graphite in the cast

iron tends to promote intergranular corrosion. The selective corrosion of the iron-rich phases opens up the structure and tends to entrap more chloride corrosion products. Wrought iron has a more homogeneous structure and the corrosion products tend to concentrate on the surface of the material.

CHARACTERISATION OF THE CHLORIDE SOURCE

In order to characterise the source of the chloride ions in the above experiments, the wash solutions of the various treatments were analysed for sodium, potassium, calcium and magnesium ions. The Na/K ratio for the wrought iron samples was 0.69 ± 0.63 which is much lower than typical values of 28.3 for normal sea water¹⁰ and is consistent with the chloride ions being in association with the iron corrosion products and little or no contamination with sea water. The Ca/Mg ratios were 0.63 ± 0.18 for the wrought iron wash solutions compared with average sea water values of 0.32. Given that the wrought iron samples were deconcreted mechanically, it is probable that the higher calcium levels are associated with traces of concretion. The cast iron wash solutions gave Ca/Mg ratios of 17.3 ± 3.2 which are typical of the outer white concretion zone described by North⁵. This result is consistent with the format of the cast iron samples which had concretion retained on one face. The Na/K ratio in the one cast iron solution analysed was 4.8 which is again consistent with the chloride ions coming from iron corrosion products, rather than from sea water.

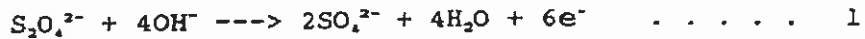
IRON EXTRACTION FROM WOOD

Degraded wood stained with iron corrosion products presents problems to the conservator dealing with the preparation of materials for exhibition. One of the typical problems associated with conservation of waterlogged timber impregnated with iron corrosion products is the major post treatment changes in the nature of the artefact. The worst problems of post conservation change is in the case where iron sulphides are oxidised to acidic iron sulphates and sulphuric acid which cause accelerated degradation of the wood¹².

Sodium dithionite is a chemical reducing agent that can reduce some of the ferric ions to ferrous ions in the FeO.OH lattice of the voluminous and pore-blocking corrosion matrix. Once some of the ferric ions have been reduced the lattice becomes unstable and much more susceptible to the complexation by the citrate ions. At neutral pH's, iron (III) has the ability to form the stable polynuclear complex $\{\text{Fe}_2(\text{OH})_2\text{citrate}_2\}^{2-}$ which has a $\log_{10}K_{\text{stab}}$ of 21.2¹¹. It is probable that the underlying cause of the efficacy of ammonium citrate solutions to complex iron at neutral pH is due to the formation of this stable complex and it is the strength of the complexes that drives the dissolution processes.

Given the effectiveness of sodium dithionite to promote the dissolution of FeO.OH , in the presence of citrate ions, a sample of naturally aged, iron-impregnated drift wood was immersed in the solution mixture where the initial solution pH was 6.20 and the redox potential was -0.527 volts vs Ag/AgCl. The stain gradually disappeared over the period of one week and the redox potential of the solution had increased to -0.092 volts versus Ag/AgCl. The change in

redox potential is a reflection of the oxidation of dithionite and the presence of iron(III) citrate complexes in solution. It is important to allow air to circulate around the solution after the reducing action has ceased as this allows dissolved oxygen to oxidise any ferrous ions to ferric ions which form more stable citrate complexes. The pH of the solution had fallen to 5.5 in accordance with the redox equation for dithionite being oxidised to sulphate,



Care should be taken to avoid using an excess of sodium dithionite to avoid the pH of the treatment solution becoming too acidic.

In order to more fully understand the nature of the interactions of dithionite and citrate with the surface of iron impregnated waterlogged wood, two samples of oak from the *Day Dawn* were immersed in a 2% (w/v) ammonium citrate solution and a 5% (w/v) sodium dithionite solution. After the iron removal experiment was completed, the wood was rinsed (distilled water) and dried before being sectioned and analysed by FT-IR spectroscopy to ascertain if any chemisorption of these chemicals into the wood structure had occurred.

The infra-red spectra of the microtomed samples of each section indicate no absorption due to organo sulphur compounds in the infra-red region and therefore it appears there has been no absorption of the complexing chemicals. However, the absorption bands arising primarily from lignin in the 1200-1600 cm^{-1} range and absorption in the 1000-1200 cm^{-1} range due to the presence of cellulose would tend to mask the stronger organo-sulphur absorption peaks. The S-H vibrations absorb in the 2600-2550 cm^{-1} range, a region not masked by other absorbing species in these samples, but the peaks are very weak and with such dilute solutions, residual chemicals would be very difficult to detect in the wood samples with this analytical technique. Scanning electron microscopy and XRD techniques would be more appropriate for analysing possible absorption of sulphur and ammonium compounds on the wood surface. Control samples should also be examined to determine the natural variations in composition and spectra before any conclusions can be made.

Although no U_{max} values were determined on the wood samples, typical values of similar timber from the same site ranged between 150 and 490%⁷. This indicates that the condition of the *Day Dawn* timber ranges from slight to moderate deterioration. Infra-red spectra of wood can also provide semi-quantitative analysis of carbohydrate content which is an indication of the degree of degradation⁷. Only a depth of 1mm of the wood surface was analysed in total. The FT-IR spectra of the suite of microtoned wood samples, whilst indicating some carbohydrate loss, did not provide conclusive evidence regarding the changes in the degree of degradation with depth.

CONCLUSIONS

The results obtained from a series of desalination experiments on the extraction of chloride ions from wrought and cast iron samples recovered from a similar marine environment have shown that a combined aqueous solution of 2% (w/v) ammonium citrate and 5% (w/v) PEG 400 at neutral pH appears to be a suitable storage medium for wood/iron composite artefacts. However, the presence of an appropriate corrosion inhibitor is required. Electrolysis in 2% (w/v) ammonium citrate solutions definitely improves the efficiency of the extraction process in this desalination solution however further work is required to establish the most suitable current densities and voltages for electrolysis of iron in intimate contact with waterlogged wood. The use of dithionite in association with aqueous citrate solutions at neutral pH was shown to be very effective in removing iron corrosion products from iron-impregnated timber and it appears that these chemicals are not residual on the wood surface.

ACKNOWLEDGEMENTS

Dr Geoff Richardson and Jeffrey Beng from the Chemistry Centre of Western Australia are gratefully acknowledged for performing and interpreting the FT-IR analysis of the wood samples. The financial support of Electricite de France for provision of a research scholarship for Paul Mardikian is gratefully acknowledged.

REFERENCES

1. Emery, J.A., Schroeder, H.A. (1974). "Iron-catalysed oxidation of wood carbohydrates." *Wood Science and Technology*. 8: 123-137.
2. Cronyn, J., (1990). "The elements of archaeological conservation." Routledge, London. p 196.
3. MacLeod, I.D., Fraser, F.M., Richards, V.L. (1989). "The PEG-water solvent system: Effects of composition on extraction of chloride and iron from wood and concretion." In *Proceedings of the ICOM Conservation Working Groups on Wet Organic Archaeological Materials and Metals, Fremantle 1987*. Western Australian Museum. pp 245-251.
4. MacLeod, I.D., Brooke P., Richards V. (1991). "Iron corrosion products and their interactions with waterlogged wood and PEG." *Proceedings of the 4th ICOM-Group on Wet Organic Archaeological Materials Conference, Bremerhaven 1990*. Deutsches Schiffartsmuseum. pp 119-132.
5. North, N.A. (1976). "Formation of coral concretions on marine iron." *Int. J. Nautical Archaeology* 5(3): 253-258.
6. Chilton, J.P., Evans, U.R. (1955). "The corrosion resistance of wrought iron." *J. Iron and Steel Inst.* p 113.
7. Wilson, M.A., Godfrey, I.M., Hanna, J.V., Quezada, R.A., Finnie, K.M. (1993). "The degradation of wood in old Indian Ocean shipwrecks." *Org. Geochem.* 20(5). 599-610.

8. MacLeod, I.D. (1988). "Conservation of corroded concreted iron." *Corrosion - a Tax Forever*. Australasian Corrosion Association. Vol 1, 2-6: 1-9
9. Carpenter J., MacLeod I.D. (1993). "Conservation of corroded iron cannon and the influence of degradation on treatment times". *Preprints of 10th ICOM Committee for Conservation, Washington, August -in press.*
10. MacLeod, I.D. (1982). "Formation of marine concretions on copper and its alloys. *Int. J. Naut. Arch.* 11(4):267-275.
11. *Stability Constants Supplement No.1, 1971, Special Publication 25, Chemical Society, London.*
12. MacLeod, I.D., Kenna, C. (1990). "Degradation of archaeological timbers by pyrite: Oxidation of iron and sulphur species". In *Proceedings of the 4th ICOM Group on Wet Organic Archaeological Materials Conference, Bremerhaven 1990. Deutsches Schiffahrtsmuseum.* pp 133-143.

Ian MacLeod: This is the whole thing with these complex composite problems. What you have to do is get into the heart of it, think of what it is like, being there trapped, as an iron corrosion product. You have iron III sitting on the surface preventing ferrous chloride from leaving the iron. What staggered us, with the massive oak timbers from the "Gilt Dragon" wrecked in 1656 is that you have bags of iron. The timbers looked like a rust bucket rather than wood. We put this in a PEG citrate/dithionite mixture. This wood had been sitting in a storage tub for fourteen years and you would have thought after that time that all the iron corrosion products on the inside would have oxidized and the wood would be ruined. Once you got rid of the red iron layer which only went in for a couple of millimetres the ferrous chloride just poured out. What we find is that once you get that initial cleaning and opening up of the wood you bump your PEG levels up to about 20% because that also acts as a complexing agent.

Molly Carlson: Do you think that solution would work as a spray?

Ian MacLeod: No, with the spray you would probably have too much oxygen with the dithionite to get it kicking off. No, what I would do is paint the solution on, then when it has done its initial chemical reduction I would use a spray. You may have to do a two step process to get it going.

Judith Logan: What concentrations of sodium dithionite were you using? We have used this to remove stains from pH sensitive materials, such as textiles. We have also tried using DTPA as a wash afterwards, as a complexing agent. I am a little curious about the toxicity of sodium dithionite and its stability at different pH's.

Ian MacLeod: Yes, you really have to watch the pH with the dithionite because what it loves to do in anything sniffing of an acid solution is to disproportionate and you get blooms of beautiful yellow sulphur. If you want to make sulphur it is an easy way of doing it. Also, you get nasty SO₂ coming off and if you smell it, it stinks. In large amounts you need to have a well ventilated area, or if you are doing the early stages of the dithionite treatment do it in the fumehood. We use the commercial grade because it is cheap, but it does stink.

Ian MacLeod: If I could add a comment on the previous paper. I think one of the blessings now that I think of it when we were doing the "Batavia" and other timbers is that we stirred our tanks by sparging them with nitrogen. Now we know why the PEG hasn't totally fallen apart because we were excluding the oxygen from it. The iron corrosion products that were being extracted by the PEG formed a nice protective scum on the surface of the PEG tank. That is also very effective at stopping oxygen from coming in. Our dirty housecleaning methods have actually helped to preserve the PEG.

Janet Hawley: I assumed you were using the dithionite-citrate PEG solutions at room temperature?

Ian MacLeod: Yes.

Janet Hawley: Did you ever use elevated temperatures?

Ian MacLeod: No, the whole problem is that at elevated temperatures bugs tend to take off. If you are getting, with the biocides that you have in your solution, control of biological attack I don't like to try and push it. Also it costs money to heat things.

Risë Taylor: What was the percentage of sodium dithionite? What is your recipe?

Ian MacLeod: It will work with something as small as 0.5% weight. It really doesn't matter how much you have there, it is just a small concentration. Just enough if you put in your platinum electrode to read the redox potential of the solution. If you get down to an EH at neutral pH of about - 0.3 you get your reaction. So you can always tell whether you have enough there. After the dithionite has consumed the oxygen in the water, which takes a few minutes, you would find redox potential in the solution falls down and sits there for half a day or a day and then gradually goes up as the dithionite gets oxidized by the air. Once it has done its few hours of work the rest of the brew just takes over and keeps going.

