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IRON CORROSION PRODUCTS AND THEIR INTERACTIONS WITH WATERLOGGED WOOD AND PEG

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ABSTRACT

The removal of iron corrosion products from waterlogged wooden and composite objects is an essential step in the long-term preservation of the organic matrix. Part of this process involves a study of the nature of the interactions of both primary and secondary iron corrosion products with both cellulosic and lignin fractions. We report the results obtained using a variety of techniques including *in situ* pH and Eh (redox potential) measurements, dissolved oxygen and capillary gas chromatographic analysis of wood extractives from iron-impregnated archaeological timbers.

These studies have established a clear link between the degree of degradation of timber, as measured by the maximum water content and the *in situ*, surface pH. The interdependence of pH and Eh in timber profiles shows that hydrolysis and redox equilibria between iron (II) and iron (III) are dominant factors in determining the interactions of wood with corrosion products. The nature of the interactions of different molecular weights of polyethylene glycol with iron corrosion products in waterlogged wood are also discussed.

A series of experiments involving PEG solutions and a variety of chelating agents under neutral and mildly acidic conditions has demonstrated the beneficial effects of heating, stirring and "chemical surface activation" in the removal of iron from archaeological waterlogged timbers. The results provide a new route for the effective extraction of iron from waterlogged organic archaeological materials.

INTRODUCTION

The problems of conserving waterlogged wood have been addressed by a wide variety of research workers over the past decade and the results have been summarised in recent conference proceedings¹⁻³. One area of particular importance is concerned with waterlogged organic materials that have been contaminated by iron corrosion products. The contamination generally arises from either direct contact with a source of corroding iron that forms an integral part of the object, as in composite pulley systems, or by association in the archaeological context. The mechanism of how iron compounds interact with wood has been extensively studied in laboratory and building site conditions^{4,5}, but the long-term effects of several centuries of immersion in a damp environment are poorly documented.

Since corroding iron in a warm marine environment is rapidly covered with a "protective" layer of calcareous concretion⁶ it can develop a significantly different micro-environment from that of the surrounding seawater since the concretion acts as a semi-permeable membrane^{7,8}. A composite iron-wooden object can therefore be subject to the long-term effects of a mildly acidic (pH 5.0±0.4) highly saline (1.5M chloride) environment if the encapsulating marine growth covers the object. Depending on variables such as the depth of sediment, temperature and water movement the primary iron corrosion product, ferrous chloride, can be precipitated as an

iron sulphide under anaerobic conditions or as an iron (III) oxy-hydroxide under an oxidizing regime. The problems of oxidation of the iron sulphide pyrite (FeS_2) in PEG impregnated archaeological timbers is the subject of recent reports^{9,10} and will not be discussed in this paper, which is primarily concerned with iron impregnated and aerobically degraded archaeological wood. Since the presence of the redox couple Fe(III)/Fe(II) is known to assist the radical breakdown of timber components in the presence of molecular oxygen it was deemed essential that we gain an understanding of the micro-environment of the timber. A knowledge of parameters such as the redox potential, the *in situ* pH and water content are of assistance in understanding the problems associated with both the mode of degradation and the removal of iron corrosion products.

EXPERIMENTAL

Surface pH measurements were made using a flat membrane combined pH electrode (Activon 412), which had an o.d. of 12.5 mm. Electrical connection between the sensing membrane and the internal silver chloride reference electrode was effected through two ceramic plugs located in the diaphragm mount surrounding the glass bulb. The pH readings were obtained with either an analog Pye 304 portable meter or with a Crison 506 or Watson Victor 5003 digital pH meter. The redox potential measurements were made using a platinum wire electrode (1.2mm diameter) and either a saturated calomel or saturated silver/silver chloride reference electrode, which had been calibrated against a standard (a quinhydrone saturated solution in a pH of 4.0). All voltages reported have been corrected to the standard hydrogen electrode unless otherwise noted. The inorganic reagents, except sodium dithionite, were of Analytical Reagent quality while the PEG and tannic acid were as supplied by the manufacturer (ICI Organic Chemicals Division). Each core was weighed prior to soaking, in water. The extractive core pH measurements were made after the 3.86mm diameter core sections had soaked in distilled deionized water for three hours. Each core was subsequently oven-dried at 110°C . The samples were then cooled under standard conditions (in a desiccator with dried silica gel) before the final weight determination. The resultant weight loss was recorded as wt% H_2O using the oven-dried core weight as the reference.

WATER CONTENT AND pH

Investigations of the parameters determining the corrosion of iron in wood have shown that the natural acidity of the timber can have a marked effect on the corrosion rate³. Depending on the wood species, there is quite a range of surface pH's observed in kiln-dried wood. Laboratory reference samples gave a mean surface pH value for red oak (*Quercus rubra*) of 4.53 ± 0.10 , white oak (*Q. alba*) 4.36 ± 0.06 and a Japanese oak sample gave a pH of 5.01. A range of *Larix* sp. have also been measured with typical values for European larch (*L. decidua*) 5.07, Western Larch (*L. occidentalis*) 5.15 ± 0.21 and Eastern Larch (*L. laricina*) 5.63 ± 0.70 . The typical moisture content of these reference samples was 20 ± 5 wt%.

In order to see what range of pH could be found within air-dried and archaeological timbers it was decided to drill cores and measure the pH as a function of depth of core from the surface environment and also to determine the corresponding range of hydration expressed as wt% water. Since the activity of both the ferrous and ferric ions will be very dependent on the local pH and water content, the corresponding localized corrosion rates are also dependent on the same parameters. It is therefore readily apparent that in order to successfully develop a proper conservation treatment programme we need to know the range of wt%, pH and Eh of the samples.

Undegraded Timber: pH and wt% H₂O

In order to gauge the significance of pH and degradation (as measured by wt% water) profiles observed in archaeological samples, it was decided to core some undegraded hardwood which had recently been felled eight months after the tree had died. The native Australian timber chosen was *Grevillea Robusta*, more commonly known as silky oak on account of its similar appearance to European oakwood. The cores were taken using a hand corer of 4 mm internal diameter. A typical plot of the pH values of the core samples after a four hour soak in distilled water is shown in figure 1 in association with the corresponding values of wt% water. Several points are immediately apparent. Firstly, in the initial 50 mm depth from either side of the roughly circular branch the average water content is 17 ± 5 wt% while the inner 80-90 mm has a much higher value at 65 ± 10 wt% H₂O. Secondly, the general trend for the pH of the cold water extractable material was that it was a mirror image of the wt% water, viz, as the wt% water increased the pH decreased. Although the scatter of the points is considerable the data shows that both the water profile and the pH profile tend to be distributed about the geometric centre of the wood rather than being centrosymmetric around the heart of the branch which was 130 mm from the start of the core and only 55 mm from the opposite side of the cored section.

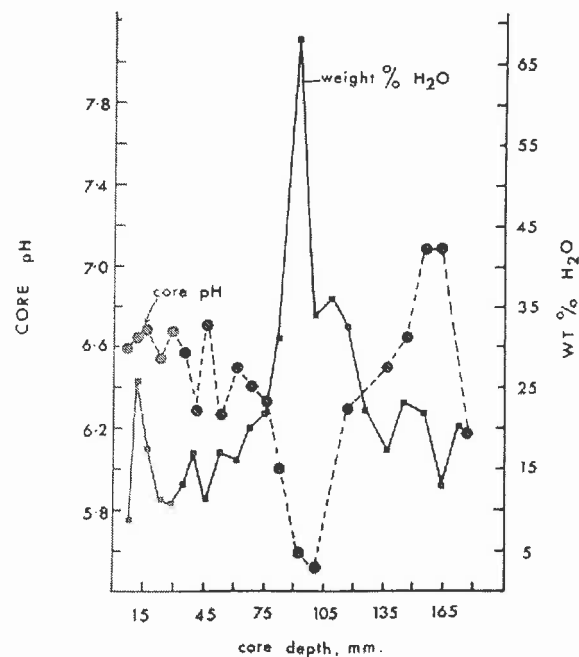


Fig. 1: Plot of core pH and wt% water against core depth for seasoned and undegraded *Grevillea Robusta*.

The timber had air-dried under ambient conditions with its bark layer intact and the varying values of wt% water shown in the profile in figure 1 are consistent with normal outward diffusion of water. Three core samples were taken to check the reproducibility of the technique which, like all coring procedures, is subject to contamination of one section with another through capillary forces and the pressure needed to bore the hole. The mean range of pH observed was 1.58 ± 0.17 units and the mean range of the corresponding water contents was 63.2 ± 3.5 wt%. In other words, the coring and subsequent measuring techniques were reproducible within a range of 10% of the mean values. The moist centre of the timber was up to a maximum of fifty-six times more acidic (Δ pH 1.75) than the outside drier portions. Because of the different chemical composition of the "white" (rapid growth) and the "red" (slow growth) rings there is naturally a

reasonable scatter of the pH and wt% water data. However, there is a linear relationship between pH and wt% which follows the general equation

$$\text{pH}_{\text{core}} = aW + b \quad \dots(1)$$

where W is the weight % water in the core sample and b is the intercept at zero wt% water. The mean value of the slope, or "a" value, for the three core samples from the Silky Oak sample was -0.0240 ± 0.0022 pH/wt% and the intercept pH was 6.92. The slope can be regarded as a measure of the sensitivity of core pH to changes in wt% water. The reciprocal of the slope (42 ± 5 wt% pH^{-1}) states the water content necessary to effect a change of one pH unit.

Waterlogged Oak Wood: pH and wt% H₂O

Recently some large ships timbers from the wreck of the *James Matthews* (1841) were recovered during dredging operations after 148 years of immersion in Cockburn Sound (Lat. 32°08.0'S, Long. 115°44.5'E), under a 2-3 m layer of sand. The vessel was built in France c1820 as the slave trader the *Don Francisco* before her capture by the English and her subsequent resheathing and refitting as a merchant barque¹². The wood was cored within three weeks of recovery during which time it was stored wet in salty tap water. The core was drilled into the side of the timber to obtain the maximum length and a combined plot of core pH and wt% water against the core depth is shown in figure 2.

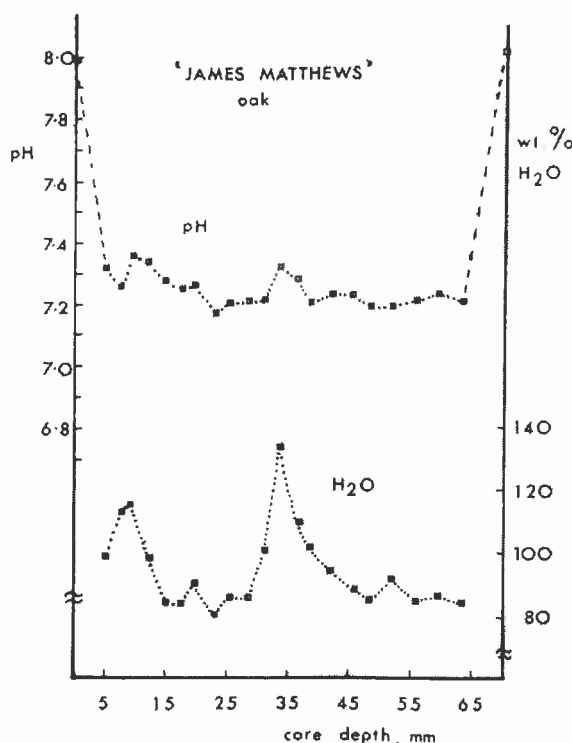


Fig. 2: Plot of core pH and wt% water for waterlogged oak wood from the *James Matthews*.

One immediately apparent difference between the behaviour of the waterlogged oak and the seasoned timber is that the *James Matthews* core pH increases with wt% water whereas the reverse response was previously noted with the undegraded wood. Since the pH of the seawater environment had been 8.1 ± 0.1 , the higher pH with higher water content is probably

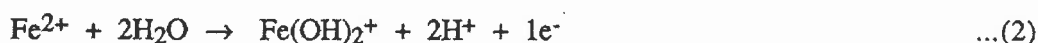
just a simple reflection of a larger amount of alkaline pore water. The *James Matthews* pH and wt% water graphs are subject to the 'error' associated with ingress of seawater through nearby toredo worm holes. Generally, the wood has a lower wt% water in the centre, but one side of the timber is generally more degraded than the other, viz. the wt% water vs core depths are not centrosymmetric. A plot of core pH with wt% water showed a linear correlation that followed the same format as that defined in equation 1 for the silky oak except that it had a different polarity, i.e. the core pH increased with wt% water for the *James Matthews* timbers. The different responses are probably due to the fact that the readily hydrolysable acidic residues have been lost from the waterlogged wood after 148 years and that the buffer capacity of the seawater is sufficient to overcome the inherent acidity of the timber. The minimum acidity observed in the centre of the core had a pH of 5.78 (see Table I) compared with seasoned white oak values of 4.36 ± 0.06 . The mean value of the range of pH observed in the cores was 0.59 ± 0.11 while the mean range of water contents was 74 ± 8 wt%.

Concreted Iron Impregnated Waterlogged Wood: pH and Eh

A number of larch "billet boxes" were recovered from the wreck of the *Vergulde Draeck* (1656) in 1982 and stored in fresh water. The boxes were built to carry flat metal strips of wrought iron to the Indies and measured 3.0x0.20x0.16 m. The iron metal was extensively corroded and the oxidation products had permeated the timber which contained up to 9.6 wt% iron (based on the wet weight of the wood). Owing to the massive amounts of loose iron from broken boxes, many of the sections were recovered with layers of red-brown iron (III) coralline encrustation on them. A section was drilled at a 45° angle to the plane of the 20 mm thick timber to give an effective core length of 28.3 mm. Owing to the hard and crumbling nature of the concretion layer and corrosion product matrix, a 12.5 mm diameter hole was drilled and the surface pH of the exposed material was recorded directly. A measurement of the redox potential was subsequently taken.

The surface pH of the concretion was that of the storage water (7.0), but as the hole was drilled the pH values swung between a maximum of 8.58 and a minimum of 5.94 some 8 mm into the matrix. The pH fell from the maximum value observed at 15 mm from the surface by 0.17 pH units per mm until the wood surface was reached. As the wood was drilled the pH increased to 8.32 and then fell semi-erratically to 6.16 at the interface with the corrosion matrix. By way of comparison, undegraded and seasoned European Larch had a surface pH of 5.07. The range of pH in the Fe₃O₄ matrix was smaller, varying from 6.49 to 5.83.

When the surface pH and the redox potential (Eh) are plotted against each other there are clearly defined relationships for the wood and the corrosion matrix, but not the concretion. In the iron impregnated wood the following equation describes the relationship between Eh and pH, viz.

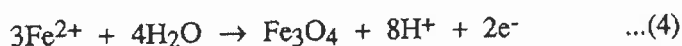


where E°, the standard reduction potential has the value¹³

$$E^\circ = 0.191 - 0.1182 \text{ pH} + 0.0591 \log \frac{[\text{Fe}(\text{OH})_2^+]}{[\text{Fe}^{2+}]} \quad \dots(3)$$

In other words, the Eh falls by 118.2mV for every unit increase in pH. The relative oxidizing power of the corrosion products are determined by the equilibrium between oxidation and partial hydrolysis of the ferrous ion (equation 2). Measurement of the voltage at the platinum

electrode indicates that the equilibrium is largely favouring the presence of $\text{Fe}(\text{OH})_2^+$ in the red iron-stained larch wood. The equilibrium is sensitive to pH changes and so a small change in pH will change the hydrolysis equilibrium and thus lead to changes in Eh. In the corrosion product matrix the dominant equilibrium is:



where the corresponding E° is given by the expression¹³

$$E^\circ = 0.980 - 0.2364 \text{ pH} - 0.0886 \log [\text{Fe}^{2+}] \quad \dots(5)$$

In short, what we have is an equilibrium between the primary corrosion product, ferrous chloride and its oxidation to the very stable mixed valency iron oxide magnetite (Fe_3O_4). From the fourfold increased response of the electrode potential to pH, compared with simple acid-base equilibria, it can be seen that when magnetite is formed from ferrous solutions the redox potential is going to be very responsive to pH. This sensitivity will naturally affect the way the wood chemistry responds. Under the combined influence of the 23 cm thick concretion layer and the 20 mm of timber, the effective oxidizing power of the turbulent seawater on the wreck site (Lat. $31^\circ 13.5'S$, Long. $115^\circ 21.5'E$) has been diminished since magnetite is the most commonly found iron corrosion product under conditions of limited supply of oxygen⁶.

Iron Impregnated Waterlogged Oak Wood: pH and wt% water

A sample of iron impregnated oak wood from the *Vergulde Draeck* wreck site was recovered in 1972 after 316 years on the seabed. It was stored in tap water until sampled in 1989. The sample had a circular hole through it where it had lost an iron bolt. During the coring it was noted that some of the timber was very extensively degraded.

The surface pH reflected the storage environment of pH 7.40 and after an initial climb to a value of 7.7 at a depth of 13 mm the pH fell to a minimum value of 6.7 at -0.017pH/mm before rising in the last 13mm to a value of 7.25. The corresponding wt% water values of the core sections increased from 150 wt% to 250 wt% at 13 mm before increasing linearly with depth to 340 wt%. The last 13 mm of the core saw the water content fall from 340 wt% to 295 wt%.

There was a linear correlation between the extractive core pH and wt% water over the inner 54 mm of the wood sample where the pH fell by 0.0208 units/wt% water. The outer 13-15 mm of the sample at either end of the core had similar rates of changing pH with distance from the surface. The left hand side of the profile saw the pH increase at the rate of $0.033-0.002\text{pH/mm}$ from the solution value of 7.40 while on the other side of the timber the pH increased at the same rate, but from an initial lower value towards the solution pH.

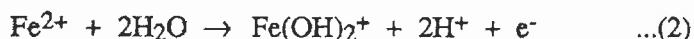
A second piece of iron-stained waterlogged oak wood from the *Vergulde Draeck* of similar thickness to the first rib was cored to check on the reproducibility of the technique. This section still contained several intact wooden treenails. The overall trend of core pH was similar to that observed in the other heavily impregnated sample described above in that there was a linear decrease in pH from a value of 7.4 at a depth of 12 mm to a minimum of 6.98 at a core depth of 68 mm and 15 mm from the far side. The two samples of timber exhibited very similar pH responses in that once the first 12-15 mm have been penetrated there is a linear response of pH with depth of the core over a distance of $50 \pm 4\text{mm}$. The second sample had a pH range over the linear region of 0.42 while the first sample covered a range of 1.04. The second sample was apparently more degraded than the first since the core sections varied from 480-210 wt% water (see Table I). There was a roughly linear correlation between core pH and wt% water with pH decreasing by 0.0017 units per wt% water. Inspection of the data in Table I shows that this is

very similar to the values obtained for the first sample. The similar behaviour of these two samples of oak from the same wreck site indicate that even though differences in degree of degradation occur the overall behaviour is the same

Iron and PEG Impregnated Waterlogged Oak Wood

Two pieces of oak timber from the *Vergulde Draeck* had been undergoing conservation treatment using aqueous solutions of PEG 800 for twenty-one months. During this time the concentration of PEG 800 was gradually increased to 25%wt/vol and the iron concentration was regularly measured. Details of the extraction kinetics are reported separately¹⁴, but each timber had released 0.19 wt% iron and 0.008 wt% chloride (based on the waterlogged weight of the artefact) at the time the cores were drilled.

Initial measurements of pH and Eh were performed on both timber samples using the drilled core method of surface in situ pH/Eh measurements. The results were similar to those obtained on the concreted larch wood in that the profiles tended to follow a "peak and trough" format since the measurements are specific to the local area and are not the average values obtained in the extracted core method. It was noted that areas of lower pH (more acidity) closely correlated with peaks in the redox potential. Plots of Eh vs pH showed that the dominant equilibrium determining the redox potential in the PEG impregnated wood had a pH dependence of 118mV per unit change in pH. This is consistent with the equilibrium being described by equation (2).



Small changes in pH can bring about significant changes in the combined equilibrium involving oxidation and concomitant hydrolysis of the Fe (II) corrosion products. Since the effects of PEG on all the iron redox equilibria have not been fully quantified we cannot calculate the true activity of the iron in the wood, but with a typical Eh of +0.290 volts at a pH of 7.2 the redox potential is defined by the equilibrium between Fe^{2+} and $\text{Fe}(\text{OH})_2^+$ as described above in equation 2¹³.

The wood cores showed similar behaviour to the iron impregnated untreated oak wood from the *Vergulde Draeck* in that once the core had penetrated the outer 15 ± 4 mm of timber there was a linear response of pH with the depth of the core over a distance of approximately 40 mm as shown in figure 3. The rate of change in pH varied in proportion to the difference between the maximum and minimum values. Although the absolute values were 0.037pH/mm and 0.018pH/mm they become 0.019 and 0.018pH/mm when divided through by the differences observed in the pH profile. When the same procedure is carried out on the non-PEG treated oak wood from the *Vergulde Draeck* the rates were 0.017 and 0.016pH/mm. It can be seen that the presence of PEG 800 does not affect the ability of the oak wood to maintain a pH gradient across a considerable thickness of timber.

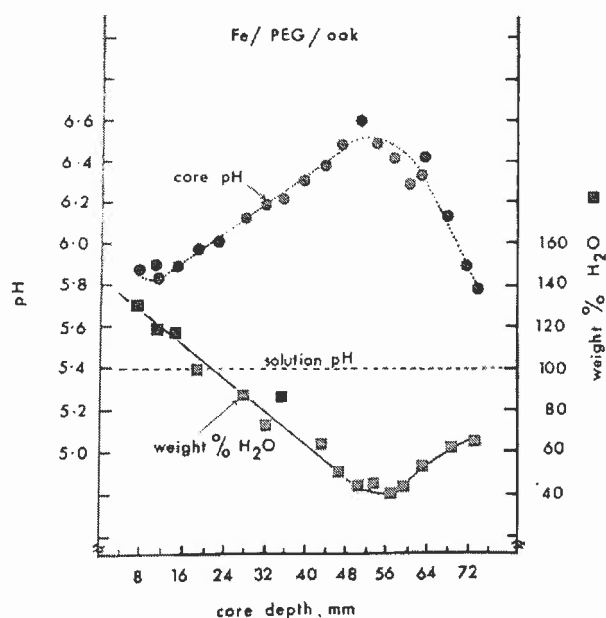


Fig. 3: Plot of core pH and wt% water for iron-impregnated and PEG-treated waterlogged oak from the *Vergulde Draeck*.

SUMMARY OF EFFECTS OF PEG AND IRON IMPREGNATION ON pH PROFILES

The presence of PEG 800 in the timber does not appear to significantly alter the way the iron-impregnated waterlogged oak responds to changes in external pH of the wash solution. However, when we look at the sensitivity of the core pH to wt% water in the sample there is a significant difference in the response between iron-impregnated wood in water and in aqueous solutions of PEG 800. Inspection of the slopes of the pH vs wt% H₂O graphs summarised in Table I shows that the PEG-impregnated wood is four times more sensitive to changes in pH than is the untreated wood, i.e. a change of one pH unit required a difference of 108 wt% water in the PEG treated wood compared with 444 wt% for the untreated iron-impregnated oak.

Separate experiments involving measurements of the Eh and pH of freshly prepared PEG solutions¹⁴ show that 25 wt% PEG 800 has a pH of 3.5 with an Eh of +0.330 volts whereas the corresponding solutions of PEG 1500 have a pH of 5.7 and PEG 400 has a pH of 6.2. The moderately strongly oxidizing nature of the solution is due to the presence of dissolved oxygen. The "natural acidity" of the PEG 800 solutions in the concentration range 6-5%wt/vol indicates that the PEG 800 has penetrated the 70 mm thickness of the timbers and that it is this property that is responsible for the different sensitivities of the wood to the wt% of water. A measure of the ability of the timber samples to buffer themselves against external changes in the pH of the wash solutions can be seen in diagrammatic form in figure 4 where the difference between the solution pH and core pH is plotted against the acidity of the storage environment. The mean values were obtained by averaging the pH values determined for each few mm lengths (20±5 readings for each core). For multiple cores of the same sample the mean values differed by no more than 0.18 units. Inspection of the plot in figure 4 shows that the buffer capacity of the timber core is given by the expression

Table I: Response of core pH to the degree of degradation of Archaeological and seasoned timbers

Wreck Site	Wood Type		Wt% H ₂ O		Core pH		+a pH/wt%	Intercept
			mean	S.D.	max	min		
	Silky oak		40	22.5	7.70	5.50	-0.024	6.93
<i>James Matthews</i>	Oak wood	#1	92	15	7.65	7.14	+0.0067	6.97
		#2	60	16	7.70	7.01	+0.0049	7.10
<i>Vergulde Draeck</i>	Larch		-	-	8.32	6.16	-	-
	Oak wood	#1	305	67	7.70	6.66	-0.0028	7.95
		#2	390	116	7.40	6.92	-0.0017	7.87
	Oak wood (PEG 800)	#1	90	39	6.62	5.80	-0.0075	6.90
		#2	132	53	7.18	5.26	-0.0109	7.88

+ 'Slope' or "a" values of the equation 1 showing the sensitivity of the timber to changes in pH with wt.% water.

$$\delta p\text{H}_{\text{core}} = -0.59 p\text{H}_{\text{solution}} + 4.13 \quad \dots(6)$$

where $\delta p\text{H}_{\text{core}}$ is defined as $(p\text{H}_{\text{core}} - p\text{H}_{\text{solution}})$. It can be seen that there is no buffering capacity when $p\text{H}_{\text{solution}} = (4.13/0.59)$ or 7.0 and that the waterlogged wood responds to only approximately 60% of the change in external pH. The lack of any buffering capacity at pH of 7.0 is only to be expected since both H⁺ and OH⁻ have the same activity at that pH.

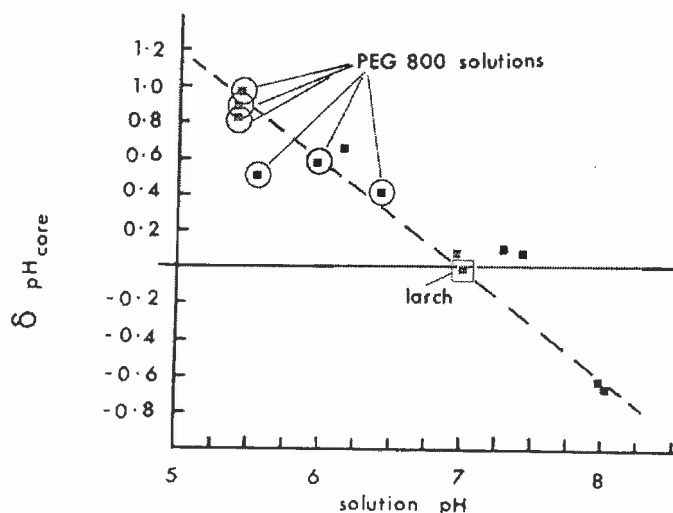


Fig. 4: Plot of the difference between core and solution pH of waterlogged wood against the storage pH.

The different rate and direction of response of core pH with wt% water of the *James Matthews* oak wood compared with the oak from the *Vergulde Draeck* can be seen as being due to two factors. The first is that the wood from the former wreck is saturated with alkaline seawater and secondly that it is much less degraded, as measured by the much lower mean water contents of 92 and 60 wt% compared with the *Vergulde Draeck* values ranging from 305-430 wt% (see Table I). The lower deterioration of the former site is due to the shorter period of immersion (148 years c.f. 316 years) and the essentially anaerobic nature of the *James Matthews* site.

DISSOLUTION OF IRON CORROSION PRODUCTS

Previous studies on the extraction of iron corrosion products in aqueous- PEG solutions¹⁵ had indicated that a 5 wt% solution of PEG was optional as far as the rate of extracting iron compounds was concerned. In order to ascertain the factors determining the rate of removal of iron a series of experiments on sections of iron-impregnated larch from *Vergulde Draeck* billet box were instigated. The sections had surface areas of $95 \pm 10 \text{ cm}^2$ and weights 65.5 ± 10.9 grams.

Effect of Stirring

Two samples of larch were placed in ten litres of 5 wt% PEG at 60°. One sample was stirred using the impellar of a thermostatically controlled bath while the second solution was still and heated by convection.

At the end of sixteen days the stirred solution had extracted twice as much iron as the unstirred sample. Analysis of the rate of iron extraction indicated that the stirred sample showed an approximately linear increase in iron concentration with $\log t$ (t is the time in hours) whereas the unstirred release rate was linear with $t^{1/2}$. The dependence on $\log t$ of the stirred solution indicates chemical control while the $t^{1/2}$ response of the unstirred indicates diffusion control. Providing that the cost of installing stirring apparatus is not prohibitive, there are obvious advantages in using agitated impregnation tanks.

Effects of Temperature

In order to determine what effect heating has on the rate of extraction of iron corrosion products, three samples of the iron impregnated larch wood were immersed in 5 wt% PEG 800 at 60°C and a control was kept at room temperature ($22 \pm 2^\circ \text{C}$). The experiment ran for two months during which the one litre reaction solutions were regularly sampled and analysed for both iron and chloride. Since the samples had varying weights, the results are discussed in terms of the normalised release rates by correcting for the geometric surface area of the object. Previous studies¹⁵ have shown that this procedure is a useful method of standardization of kinetic data on museum artifacts.

The iron release rates were linearly dependent on $t^{1/2}$ (the square root of the reaction time) for both sets of data. At 60°C the iron extraction rate was $162 \pm 4 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1/2}$ whereas at 22°C the rate was $18 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1/2}$. Although two of the 60°C samples had an induction period of about seven hours which was followed by a higher rate of $206 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1/2}$, the overall rates are based on the total length of the experiment. After two months, the 5 wt% PEG 800 at 60° had removed $58 \pm 11\%$ of the total iron content of the timber samples whereas the room temperature control had extracted only 3.7%. In absolute terms the 60°C treatment removed

1.49±0.13 gram of iron while the room temperature sample extracted 0.19g or a factor of 7.8 times less iron.

The amount of chloride removed during the same treatment procedure was relatively small owing to the previous seven years of soaking in tap water. However, it is interesting to note that the room temperature extraction removed 0.15 wt% chloride compared with 0.090±0.026% at 60°C. At elevated temperatures it is possible that corrosion product phase transitions occurred which retained more chloride in the matrix. This is supported by the fact that all room temperature experiments with a variety of complexing agents extracted the same amount of chloride ions (0.17±0.07 wt%). After two days at 60°C the stoichiometry of the extracted iron and chloride was 1.15±0.27 iron atoms per chloride whereas after fifty-nine days it had increased to 20.0 ±7.4. By way of contrast, the corresponding ratios at room temperature were initially 0.34 iron per chloride and finally a ratio of 1.1:1.

The elevation of temperature brought about a marked improvement in the rate at which iron corrosion products were removed from the heavily impregnated wood. The shortening of treatment time by a factor of between nine and eight times means that serious consideration should be given to heating treatment tanks. When combined with stirring the treatment at 60°C means it is possible to achieve an improvement in the iron removal rate of up to eighteen times.

Effects of Chelating Agents

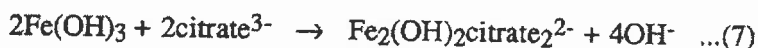
Since iron-impregnated waterlogged wood is often associated with composite wood and metal systems it is necessary to look at the use of complexing agents to help dissolve iron corrosion products. The use of mineral acids or the parent organic acids, although effective, often results in either extensive corrosion of the remaining metal or destruction of the wood.

NEUTRAL EXTRACTIONS

Although the solubility of iron (III) hydroxide at a pH of 7 is limited to $4 \times 10^{-19} \text{M}$, iron (II) hydroxide is much more soluble at the level of $8 \times 10^{-2} \text{M}$ ¹⁶. If corrosion products can be extracted at a pH of 7 the effects on wood and metal should be minimal. Knowing that significant dissolution of the FeO.OH surface minerals with citrate and oxalate cannot be achieved at such a pH it was decided to pretreat the oxidized wood and corrosion products with sodium dithionite. Enough dithionite was added to produce a reducing environment¹⁷ in the 0.25M ammonium oxalate and ammonium citrate solutions, with average pH values 6.55±0.33 and Eh readings of -0.323±0.023 volts. The effect of this "pretreatment" was most dramatic.

Ammonium Citrate

The leaching kinetics followed the expected linear dependence on $t^{1/2}$ for twenty-five days at which time a plateau was reached. The one litre reaction solution extracted 1545mg at the rate of $362 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1/2}$ compared with the control in deionized water which extracted iron at the rate of $64 \mu\text{g} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1/2}$ for two months, after an induction period of ten days. The differences in the reaction rates, a factor of 5.7, is reflected in the total amount of iron extracted during the experiment for the ratio of the percent of available iron extracted by the solutions is 61.2:11.3 or a factor of 5.4. Detailed comparisons are not possible because neither solution displayed constant behaviour. However, during the experiment these results indicate that even without maintenance of the reducing environment the addition of dithionite and citrate greatly enhances the rate of removal of iron (III) corrosion products at neutral pH. The enhanced performance of neutral citrate solutions is also due to the formation of an iron (III) hydroxy citrate complex which will dissolve Fe(OH)₃ at a pH of approximately 6.2. The dissolution process is described by equation 7 below,



The ability to form such hydroxy-carboxylate complexes appears to be limited to citric acid species.

Ammonium Oxalate

In the first seven days the oxalate solution removed 219mg of iron at the rate of $163\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1/2}$ compared with a water extraction rate of $15.4\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1/2}$. During the remaining of fifty-two days the solution concentration of iron gradually fell with the precipitation of ferrous oxalate¹⁸. In order to keep evaporation problems under control the experiments were conducted in white plastic tubs (ice cream containers) sealed with a lid, i.e. the experiments were conducted in the dark. Under these conditions the photochemical dissolution of goethite and lepidocrocite in oxalate solutions is minimized, but not enough to prevent the formation of the insoluble orthorhombic β ferrous oxalate which is apparently promoted by UV light¹⁸. The addition of the dithionite would have provided a moderate concentration of Fe(II) ions at the surface to allow formation of the $\text{Fe}(\text{C}_2\text{O}_4)_2^{2-}$ complex. The mechanism for dissolution of the iron (III) mineral involves electron transfer between the "adsorbed ferrous oxalate and structural ferric ions". This results in the oxidation of the adsorbed species and desorption of the $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ species because of its altered structure¹⁸.

At the end of the experiment the oxalate had removed only 10.8 wt% of the total iron content in the wood sample so its use at neutral pH cannot be recommended when compared with the efficacy of the citrate solution. The work of Cornell and Schindler¹⁸ has shown that the optimum pH for photochemical dissolution of goethite in oxalate solutions is at pH 2.6 under which conditions the oxalate also acts as an iron corrosion inhibitor¹⁹.

ACID EXTRACTION

The use of tannic acid solutions on composite waterlogged iron-wood composites has obvious advantages as the tannic acid acts as a corrosion inhibitor as well as a complexing agent. The natural pH of a 0.025M (42.53g/l) tannic acid solution was 2.82. At this pH the solubility of ferric hydroxide is still limited to $1.4 \times 10^{-6}\text{M}$ ¹⁴ and so the dissolution of the red-brown corrosion products is due to the complexing ability of the tannic acid. During the first week, iron corrosion products were dissolved at the rate of $190\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1/2}$, but after ten days the release rate was irregular. A total of 1098mg or 25.3 wt% of the total iron content was removed by the end of the two month experiment

CONCLUSION

The measurements of redox potential Eh and the core pH of wood samples has been shown to be a reproducible experimental procedure. The results obtained from a series of measurements on waterlogged oak and iron-impregnated waterlogged timbers has shown that it is possible to determine the dominant equilibria within the wood matrix. In an undegraded hardwood the primary cause of acidity relates to hydrolysis of acetylated residues while in waterlogged archaeological wood the pH is a mirror of the burial environment and the degree of degradation as measured by the water content. For iron-impregnated archaeological timber the dominant equilibrium involves the oxidation of ferrous ions and the concomitant hydrolysis to produce $\text{Fe}(\text{OH})_2^+$. A series of experiments with iron-stained larch wood has shown that elevation of temperature greatly enhances the rate of iron extraction by 5 wt% PEG 800 solutions and that it is further enhanced by stirring. The novel use of dithionite in association with citrate solutions at neutral pH was shown to be very effective in dissolving iron out of the timber. Not only does this discovery offer hope to waterlogged timber conservators but it also means that the same

technique could be applied to iron stained archaeological textiles. Whilst less effective, the use of oxalate and tannic acid solutions may be preferable for composite wood-iron objects because of their effectiveness as corrosion inhibitors.

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