

The PEG-Water Solvent System: Effects of Composition on Extraction of Chloride and Iron from Wood and Concretion

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Introduction

The problems of conserving composite materials have plagued conservators for many years¹. The problems are typified by those composites made of iron and wood. The storage environment that is ideal for iron, namely, dilute sodium hydroxide solutions, is extremely aggressive to wood. Whereas the storage environment for waterlogged timber, namely, that of fresh water is, without the addition of suitable inhibitors, extremely aggressive to corroded iron. As a result the treatment and storage of composite mixtures of corroded iron and waterlogged wood has had to be one of compromise.

The action of ferric ions on the hydrolysis of cellulose is well documented² and is often seen in the form of accelerated degradation of wood around corroded iron structural members³. However, the mechanism of interaction of the wood degradation products and iron during corrosion on archaeological sites is very poorly documented. A systematic study of these factors is part of our continuing investigation. One of the typical problems associated with conservation of waterlogged timber impregnated with iron is the fact that there are often major post-treatment changes in the nature of the artefact. For example, continued iron corrosion of the material within the composite structure can cause severe mechanical damage even after the object has been freeze-dried.

The worst problems of post conservation change of iron corrosion products are in the case where iron sulphides are oxidized to iron sulphates and sulphuric acid. Previous work in these laboratories has shown that the factors affecting the rate of removal of chloride ions from corroded cast and wrought iron objects have been determined⁴. This work has led to significant changes being made in the treatment methods for iron objects recovered from the sea or other chloride rich sites⁵. In order to understand the factors affecting stabilization of corroded composite wood-iron materials we investigated both the iron-impregnated concretion⁶ and timber.

The nature of the corrosion mechanism of iron in chloride-rich aqueous PEG mixtures changes with PEG concentration. There appears to be a critical amount of PEG required in the solution before the metal corrosion rate decreases to an acceptably low level. One of the major problems associated with treating composite wood and iron mixtures is to remove as much chloride as possible whilst maintaining the integrity of the waterlogged wood. In order to properly gauge how each part of the composite mixture performs, extraction experiments were carried out in a range of PEG solutions to determine which combination of water and polyethylene glycol gave maximum rate of removal of both chloride ions and iron corrosion products. It was to this end that the current study of iron-impregnated wood and concretion was undertaken.

Experimental

A sample of iron-impregnated concretion from the Xantho (1872) engine, currently undergoing electrolysis in 0.1 M sodium hydroxide solution, was removed, after fourteen months, in one integral length, by gentle percussion and sectioned into six pieces by a bandsaw⁷. One piece of concretion was placed in each of the following solutions, 0%, 2%, 5%, 10%, 20% and 40% (w/w) polyethylene glycol 1500. A wooden pulley recovered from the wreck site of the James Matthews (1841) had been stored in "fresh water" for twelve years before it was placed in deionised water and monitored for five days prior to immersion in a solution of 20% (w/w) polyethylene glycol 400 which was changed to a 20% (w/w) solution of polyethylene glycol 800 after only 129 hours of impregnation. Monitoring of this solution continued for 381 days.

Two large pieces of iron-impregnated European Oak from the *Vergulde Draeck* (1656) were recovered in 1982 and stored in tap water for three years. Prior to immersion in PEG they were monitored for one week in deionized water and then transferred 2% (w/w) polyethylene glycol 800 for 12 days. This short impregnation was followed by a 5% (w/w) polyethylene glycol 800 solutions for 98 days and finally placed in a solution of 10% (w/w) polyethylene glycol 800. The surface areas and masses of all samples were obtained before any preliminary washing treatments were implemented. After treatment began the wash solutions were normally analysed every two weeks to monitor the progress of release of chloride ions and iron species from the wood and concretion. The concentration of iron in the treatment solutions was determined by, firstly, removing known volumes of the various polyethylene glycol solutions and evaporating to dryness. Concentrated hydrochloric acid (20% w/w) was then added, heated gently and after cooling, the samples were made up to volume with distilled deionized water, prior to atomic absorption spectrophotometric analysis. No sample preparation was required for the chloride analyses. All chloride determinations were performed on a Buchler-Cotlove chloridometer automatic titrator.

Viscosities of polyethylene glycol 400, 800 and 1500 solutions were measured via a viscosity cup, BS 3900⁸. Molal volumes were calculated from data obtained by picnometer experiments and conductivities of sodium and iron (II & III) chlorides dissolved in the solvent mixtures were analysed by a Philips PW 9525 portable conductivity meter. The solutions were not thermostated, but the above measurements were obtained under constant laboratory temperature conditions of 22.5±0.5°C. Surface areas were calculated using a PLANIX 7 planimeter to determine the areas within the traced outlines.

RESULTS AND DISCUSSIONS: Extraction of iron and chloride from concretion

The first observation on inspecting the treatment solutions after five days of impregnation with various concentrations of PEG 1500 was that there were significantly different amounts of iron dissolved in the various solvent mixtures. The solutions of deionized water (<20µS) and 2,5,10,20 and 40 wt% PEG were monitored initially every few days, then every week until the intervals were extended to monthly determinations of chloride and iron concentrations by the end of the year. Because of difficulties in obtaining reliable samples for total iron determination (precipitation of iron oxy hydroxides in the impregnating liquor), the final analyses were based on the ashed contents of the solutions and precipitate. The chloride and iron concentrations were plotted against a range of time functions including linear, log₁₀ and the square root of treatment time to see if there were any uniform trends in the rate at which the ions were released. The most consistent results were obtained for correlations of concentration with $t^{1/2}$, where t is the time elapsed in hours since the inception of the experiment. Correlation coefficients for the linear regression (least squares fit) were typically 0.9964±0.0029 for chloride ions and 0.9928±0.0087 for the iron values. Linear dependence of concentration on the square root of treatment time is a characteristic of diffusion-controlled processes⁹.

A two-stage process characterizes the results, which is primarily due to the fact that the concretion had been attached to the Xantho engine under electrolysis in a 0.1 M sodium hydroxide (pH 12.5) solution for eighteen months. The molar ratio of chlorine to iron in all of the wash solutions was very high (14 ± 3) in the first few weeks and then it rapidly fell to values more consistent with normal stoichiometry, so that after twelve weeks typical values of the Cl/Fe ratio ranged between two and three. The way in which the ratios change with time for 5%, 20% and 40% are shown in Figure 1. The turning point in the ratio for the 40% solution occurs after approximately 42 days. The changeover from the initial response of the concretion to the long-term trend occurs over a month in the period of between 35-45 hr^{1/2}, depending on the concentration of the PEG.

Since electrolysis (E_h -0.74; pH 12.5) would have "immobilized" some of the iron corrosion products it is not surprising that chloride ions will tend to be selectively mobilized in the initial period when diffusion front of the new wash solution begins to penetrate the dense matrix⁶. The differences in the rate of removal of chloride ions from the concretion are shown schematically in Figure 2 and in Table 1. The data presented in Figure 2 shows that the maximum release rate for the first stage is for 5 wt% PEG and that in the second stage the maximum rate is shared by 5 and 10 wt% PEG. Since the flux of chlorides is controlled by diffusion, the chloride release rates will be dependent on surface area of the object. In order to see if the trends shown in Figure 2 are a true reflection of the 'real' rate, the apparent rates were 'normalised' by correcting for the geometric surface area of the slices of concretion. No attempts have been made to incorporate any roughness factors since the surface texture of all the samples was reasonably uniform. The normalised release rates for both stages of the

experiment are plotted as a function of PEG concentration in Figure 3. Inspection of the data in Table 1 shows that the maximum release rate occurs in the range covered by 5-10 wt% PEG. The limited number of experiments prevents precise location of the turning point.

The rate at which iron was mobilised by the neutral aqueous PEG solvent mixtures was also shown to be markedly dependent on the solvent system, viz., on the concentration of PEG. The raw and normalised data are listed in Table 2; the latter is shown schematically in Figure 4. The dependence on PEG concentration shown by the iron release rate is very similar to that exhibited by the chlorides described above. The normalised release rate for the second phase shows maximum rates in the range 5 - 10 wt% PEG. The iron release rate for the initial phase in the 20 wt% PEG solvent appears to be anomalous since it is the only one of four sets of data not to follow the general trend. For those concerned with trying to stabilize a concreted composite iron metal in an object the use of an impregnating solution in the 5-10 wt% PEG 1500 would appear to have definite advantages since this represents the maximum rate for extracting both chloride and iron corrosion products. Although this range in PEG concentrations is not optimum for stabilising the timber, prolonged immersion in such solutions will minimise many post conservation degradation problems.

Monitoring the weight of all the concretion samples shows that there is a general increase for the first two months but then the weight begins to fall at the same time as the rate of removal of iron and chloride increases (see Figure 2). The higher PEG-water mixtures such as 20 and 40% take longer to reach the turning point, which suggests that the mixed solvent diffuses into the concretion at a slower rate than mixtures such as 2, 5 and 10%. Since the diffusion gradient is dependent on the ratio of the concentrations of PEG across the concretion ($\Delta G = -2nRT \ln \frac{a_I}{a_{II}}$, where a_I is the activity at the reacting surface and a_{II} is the bulk activity) a higher concentration of PEG might be expected to penetrate more quickly. The results of our experiments show that there are other factors determining the rate at which the solvent penetrates the concretion.

The PEG-Water solvent system

If we consider that the various concentrations of PEG 1500 (or any other grade of PEG) as being organic solvent-water mixtures then it is possible to use measurements of parameters such as molar volumes, viscosities and conductivities to study the nature of the solvent system. The terminal hydroxyl and the ethoxy linkages in all grades of PEG are capable of hydrogen bonding, especially with water itself. The extent of the interaction is shown by the changes in the apparent molal volume of both PEG 1500 and water as the concentration of the co-solvent is varied. The apparent molal volumes (V) were calculated using the relationship

$$V = \frac{M}{d_0} - 1000 (d - d_0) / d_0 C$$

where d_0 and d are the densities of the solvent and the solution respectively, M is the molecular weight of the solute and C is its concentration in mol. per litre¹⁰. The apparent molal volumes of both water and PEG are shown in Figure 5. The greatest change in V for PEG 1500 occurs in the range 0-5% w/v PEG by comparison with the differences in V between 10% and 40% PEG. This region of greatest change in the 'size' of PEG 1500 is also the region of greatest change in the rates of both iron and chloride from the concretion. Measurements of the equivalent conductance of 0.1 M sodium chloride and 0.033 M ferric chloride dissolved in the appropriate PEG 1500-water mixtures show that the conductance decreases relatively rapidly in the range 0-5% PEG and then falls away at a steady rate as the concentration is increased up to 40 w/v% (see Figure 6). Since the conductivity is inversely proportional to the viscosity of the solution, the effect on conductance by viscosity can be estimated by studying how the Walden product ($\lambda_0 \eta$) varies with concentration. The Walden product is inversely dependent on the radius of the solvated ion

$$(A_0 n) = FeZ / 6\pi r_s$$

where F is the Faraday constant, Z the absolute ionic valence, e the electronic charge and $r_{s,1}$ the radius of the solvated ion. Measurements of the kinematic viscosity of the PEG-water mixtures shows that the viscosity goes through a minimum in the region of 2-5%, the same region where there is maximum rate of change in the iron and chloride extraction rates. As the PEG concentration increases the solvodynamic radius of both the ferrous and ferric ions will probably increase as the metal ion becomes increasingly solvated by PEG. The combined effects of increased solvent viscosity and increased size of the solvated iron (II) and iron (III) species provide a good rationalization for the fall off in release rates as the PEG concentration is increased. The effect of the lowered dielectric constant on ionization cannot be underestimated. Although the nature of iron corrosion products in objects recovered from archaeological sites has been the subject of controversy¹¹⁻¹³ there is little doubt that

the major corrosion products adjacent to the metal corrosion front under protective concretions are iron (II) chlorides. The molar ratios of chloride to iron found in the various 'solvent mixtures' has already been mentioned (see Figure 1) and is consistent with the fact that the iron concretions contain low levels of sodium (0.14 wt%) compared with iron (51.5 wt%), i.e., the chlorides are principally associated with iron corrosion products^{6, 11}. Characterization of the precise nature of the solvated iron (II and III) species has not been attempted. Where the ratio of chlorine to iron being released is high it is probably a reflection of the fact that not all the products of the interactions with the PEG-water solvent system are soluble.

Extraction of Iron and Chloride from Timber

Owing to curatorial constraints it was not possible to section the samples of iron-impregnated timber from the *Vergulde Draeck* (1656) or the *James Matthews* (1841). The pulley sheave from the *James Matthews* was found dry in its treatment container and was therefore deemed to be suitable for experimental purposes! During the experiment the sheave was rehydrated for five days then placed into a 20% (w/w) PEG 400 solution for 47 days then transferred to a 20% (w/w) PEG 800 solution for a further 381 days. A plot of the weight of the object vs. the square root of treatment time is shown in figure 7. Apart from the initial changes on rehydration the maximum change after rehydration amounted to only a 2.6 wt% increase. Also plotted on the same graph are the weights of iron and chloride removed from the pulley by the aqueous PEG mixtures. The onset of the decrease in maximum weight corresponds to the increase in the rate of removal of iron from the pulley sheave. Given that the pulley sheave had been washing for twelve years in Perth tap water (140 ± 40 ppm chloride) it is hardly surprising that once the surface salt (883 mg) had been dissolved in deionized water (during rehydration) there was very little chloride extracted. This is consistent with the observation that the major corrosion product on the surface of the timber was lepidocrocite (FeO.OH). During impregnation in the 20% PEG 400 the normalised chloride release rate was $27 \mu\text{g} \cdot \text{cm}^{-2} \text{hr}^{-1/2}$ while the corresponding value in the 20% PEG 800 was $31 \mu\text{g} \cdot \text{cm}^{-2} \text{hr}^{-1/2}$ the change in release rate is partly a reflection of the change in the viscosity of the solutions with the increase in molecular weight. The experimental value for the normalised iron release rate in the 20% 400 solution was $26 \mu\text{g} \cdot \text{cm}^{-2} \text{hr}^{-1/2}$ while the value in 20% PEG 800 was $42 \mu\text{g} \cdot \text{cm}^{-2} \text{hr}^{-1/2}$. The ratio of kinematic viscosities of 20% PEG $^{400}_{/800}$ is 1.53.

The two pieces of oak from the *Vergulde Draeck* were removed from a "tap water" tank after three years of storage and placed in fresh deionized water for six days prior to impregnation with PEG 800 in a 2% (w/w) solution for 15 days followed by a 5% solution for 98 days and a 10% solution for 276 days. The mass of the timber was regularly monitored as were the iron and chloride solution concentrations. The behaviour of both timber samples (4.8 and 4.3kg initial weight) was very similar to that of the *James Matthews* pulley sheave after it had been hydrated, viz., there was a gradual increase in weight in the 5 wt% PEG 800 solution until it reached a plateau for 28 days. A plot of the weights of the timbers vs. time gave surprisingly similar values: $19 \mu\text{g} \cdot \text{cm}^{-2} \text{hr}^{-1}$ for the pulley sheave in 20% PEG 400 and 31 and $11 \mu\text{g} \cdot \text{cm}^{-2} \text{hr}^{-1}$ respectively for the larger and smaller pieces of oak from the *Vergulde Draeck* in 5 wt% PEG 800.

The onset of the decrease in the weight of the timbers corresponded to an increase in the rate of extraction of iron. The solution concentrations were increased to 10-wt% during this period and the weight continued to fall until the rate of iron extraction had begun to tail off. As in the case of the *James Matthews* timber, the amount of chloride extracted after the first two months of treatment was negligible. The normalised iron release rates for the various solutions are summarized in Table 3. Whilst it is appreciated that the methods of estimating surface areas are crude, the general trends of behaviour for extracting iron from timber are similar to those observed with the *Xantho* concretion. Whilst the amount of iron extracted is small (0.1-0.3 wt%), the removal of these aggressive metal ions will minimize degradation of the residual wooden structure.

SUMMARY

The effects of concentration and molecular weight of PEG on the removal of iron corrosion products from wood and concretion have been studied. The results can be rationalized in terms of changes in the parameters such as the viscosity and other colligative properties of the PEG-water solvent system. Long induction periods of several months are commonly observed before significant changes occur with artefacts that have been in storage for several years. The optimum concentration of PEG for extraction of chloride ions associated with iron corrosion products from both wood and concretion

is generally in the range of 5-10% (wt/vol) PEG. Long treatment times at room temperature characterise the removal of significant amounts of iron from archaeological organic materials.

Table 1: Rate of extraction of chloride ions into aqueous PEG 1500 from *Xantho* (1872) concretion, one-litre volumes.

Concentration of PEG 1500 (% w/v)	First Stage		Second Stage	
	mg.hr ^{-1/2}	µg.cm ⁻² .hr ^{-1/2}	mg.hr ^{-1/2}	µg.cm ⁻² .hr ^{-1/2}
0%	2.2	13.3	8.6	51.9
2%	5.2	27.9	36.6	196.4
5%	35.0	119.2	82.4	280.6
10%	8.8	32.6	79.4	294.0
20%	11.8	39.2	33.8	111.2
40%	5.0	19.3	21.0	80.9

Table 2: Rate of extraction of iron into aqueous PEG 1500 from *Xantho* (1872) concretion, one-litre of wash solution.

Concentration of PEG 1500 (% w/v)	First Stage		Second Stage	
	mg.hr ^{-1/2}	µg.cm ⁻² .hr ^{-1/2}	mg.hr ^{-1/2}	µg.cm ⁻² .hr ^{-1/2}
0%	0.8	4.8	33.9	204.7
2%	5.8	31.1	51.2	274.7
5%	17.0	57.9	136.6	465.1
10%	12.0	44.4	115.2	426.5
20%	42.4	140.7	81.6	270.8
40%	7.6	29.3	19.2	74.0

Table 3: Extraction of iron and chloride from waterlogged timber.

	Total extracted		Normalised release rates	
	Cl wt%	Fe wt%	µg.cm ⁻² .hr ^{-1/2}	
			Chloride	Iron
<i>James Matthews pulley</i>	0.53	0.32	26.6*	26.1*
			30.8+	42.0 ⁺
<i>Vergulde Draeck (i)</i>	0.08	0.10	-	37.0 ^a
			34.8 ^b	34.8 ^b
			9.4 ^c	24.3 ^c
			-	21.4 ^d
<i>Vergulde Draeck (ii)</i>	0.07	0.07	-	36.9 ^a
			58.8 ^b	32.4 ^b
			13.3 ^c	22.2 ^c
			-	23.1 ^d

*20% w/v PEG 400, ⁺ 20% w/v PEG 800, ^a is water, ^b 2% PEG 800, ^c 5% PEG 800
^d 10% PEG 800

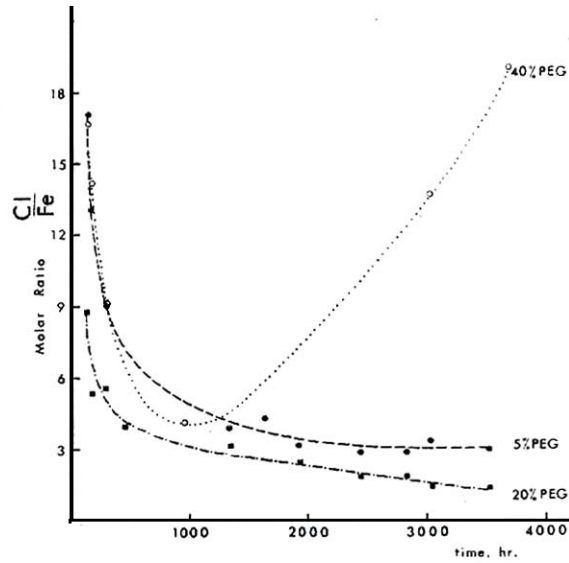


Figure 1: Molar ratio of chloride to iron in the treatment solutions for *Xantho* concretion samples versus treatment time. Polyethylene glycol (PEG) grade (ICI) 1500 – concentrations expressed as wt%/vol.

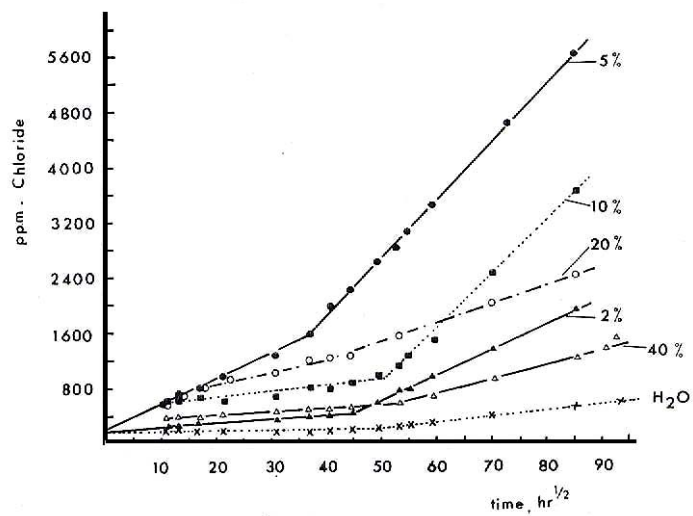


Figure 2: Chloride ion concentration in the wash solutions containing iron-rich concretion from the *Xantho* as a function of the square root of the treatment time. Concentration of the PEG 1500 is wt % vol. Solution volume corrected to one litre.

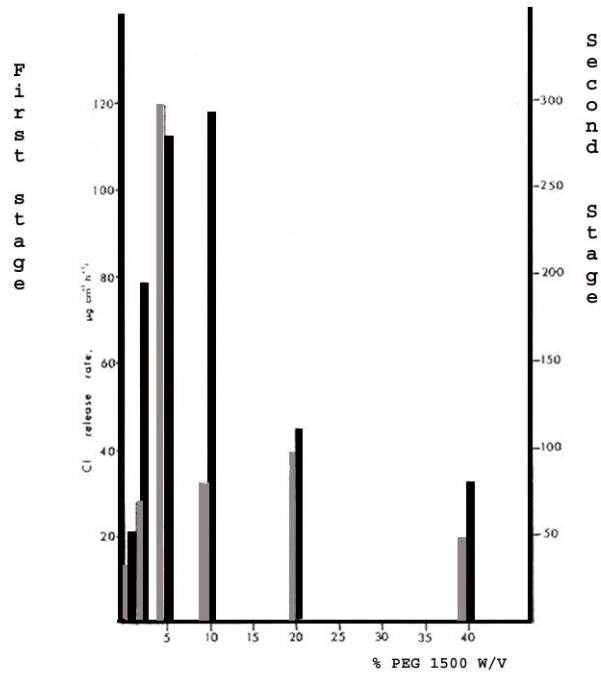


Figure 3: Plot of normalised chloride release rates in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1/2}$ versus PEG 1500 concentration (wt%/vol) for both stages of the treatment of *Xantho* concretion.

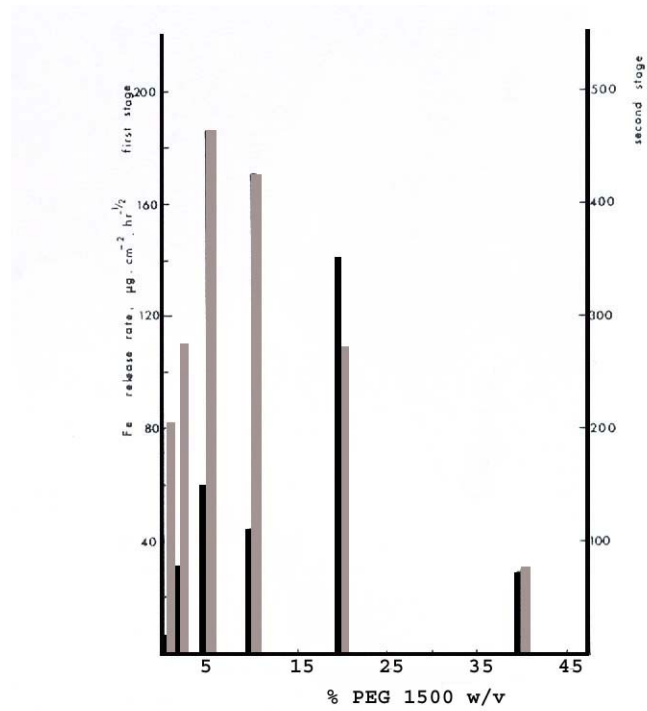


Figure 4: Plot of normalised iron release rates in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{hr}^{-1/2}$ versus PEG 1500 concentration (wt%/vol) for both stages of the treatment of *Xantho* concretion.

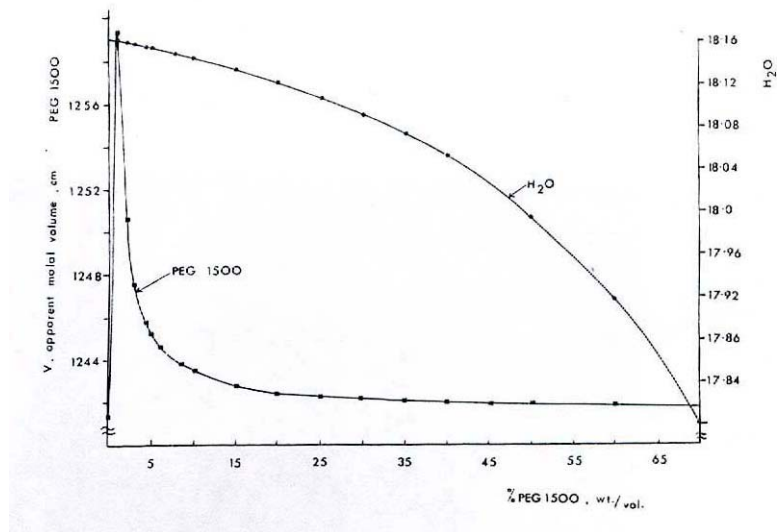


Figure 5: Apparent molal volumes of water and PEG 1500 as a function of solution composition.

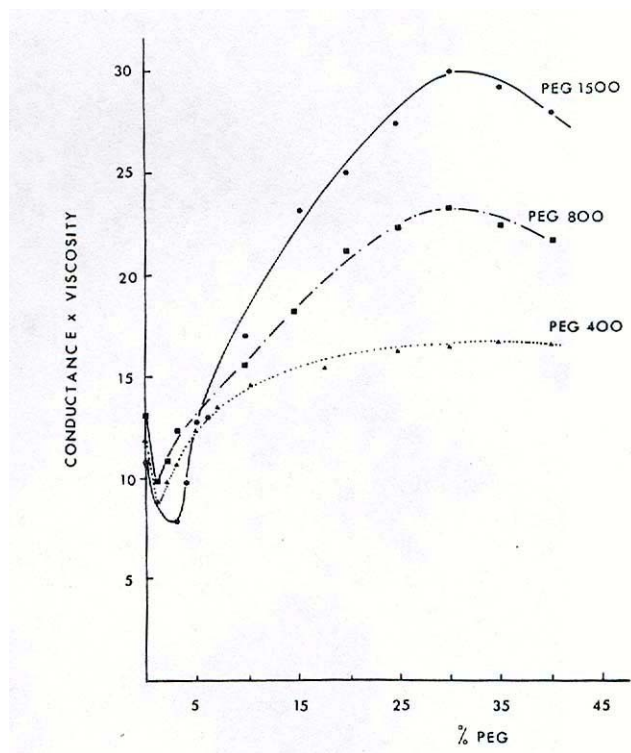


Figure 6: Plot of the product of kinematic viscosity and molar conductance of 0.1M sodium chloride versus concentration of PEG 1500, 800 and 400, expressed as wt%/vol.

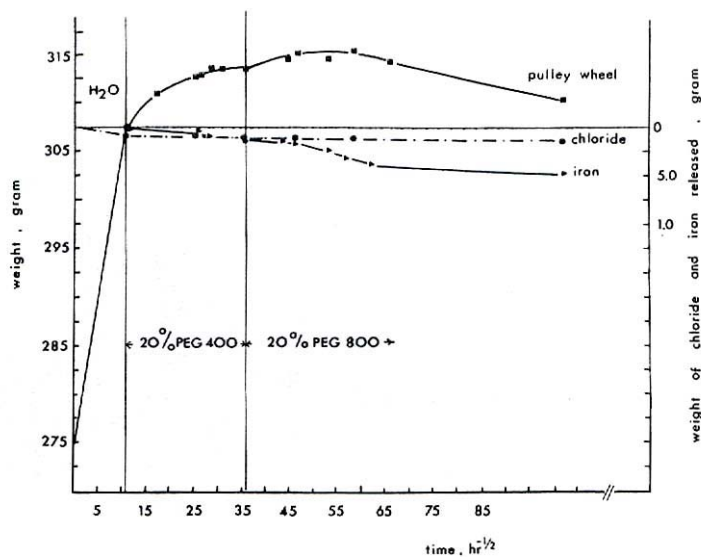


Figure 7: Plot of weight of *James Matthews* pulley and the weight of iron and chloride released into solution versus the square root of treatment time for the rehydration and impregnation phases with 20wt%/vol PEG 400 and 20wt%/vol PEG 800.

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Question: Jon Carpenter

Is it possible to use an anode in that system, instead of a carbonate?

Answer: Ian MacLeod

The problem with anodes is that you need to get good electrical contact. In the case of the *James Matthews* pulley sheave the remaining iron was extremely graphitized, so graphitized in fact that when I put my platinum electrode gently on it I left a nice little dint in the surface. If you were trying to get good electrical contact you would need some type of a screw clamp attachment and I feel that in a case like that you would damage the object. Also in the case of a small object you need to be careful, because as your anode corrodes it produces alkalinity because a portion of the corrosion process results in hydrogen evolution and so the solutions become alkaline. The anodes do not have 100% current efficiency; hydrogen evolution may amount to 15% so you would tend in a small treatment container to see big changes in pH and so you would have to be quite careful to keep an eye on the pH of the solution. It is not impossible to set up such a system, but I think you have got much more chance of protection by using appropriate chemical inhibitors and hopefully ones that aren't going to be aggressive to the wood. I think that you could probably control your iron corrosion through inhibition in case like that rather than using some form of sacrificial protection.

Question: David Grattan

I was wondering about the effect of pH on the extraction; what would happen if you increased the pH, to the rates of iron and chloride extraction?

Answer: Ian MacLeod

I think the rate would fall off because one of the problems is that you want to keep fairly neutral solutions if you can, otherwise you really run into problems. Since you are trying to mobilize the iron and the chloride they would tend, when they met an alkaline front, to reprecipitate. Consider what happens in the concretion of an iron cannon ball. The concretion forms around it and the pH of open seawater is 8.2, but the equilibrium pH inside is about 5. Now as iron diffuses out towards the seawater the change in pH is partly due to hydrolysis with dissolution of calcium carbonate followed by precipitation of the iron corrosion products. Alkaline solutions would only exacerbate the problem.

In terms of weight percent, the amount of chloride and iron removed from the concretion during the last fourteen months in which the study was going on was around about 1'-2wt%. You may not consider that is significant, but it means that you have taken out all 4, 5, maybe 10 grams of iron and 4 or 5 grams of chloride out of an object, that is only 15x5x2 centimetres. I think that is quite significant and more particularly in that the iron (III) ions that are left in the wood can have such a devastating effect on the breakdown of the wood structure. If you can get any iron out and you are doing well; if you get lots out you are doing much better. I think we have half an answer to a quarter of a question, but at least it is a first step.

David Grattan

It is a very important observation that PEG enhances the extraction of ferrous chloride

Ian MacLeod

What is happening is that even though an object has been sitting around in a treatment tank for years there is within the heart of the object, still untapped, un-bonded ferrous chloride which is just sitting there waiting to come out and all it needs is for us conservators to be the liberators and get the ferrous chloride out.

Question: David Grattan

You didn't really talk much about the mechanism, how you think that is taking place?

Answer: Ian MacLeod

I am not exactly sure of the mechanism.

Question: David Grattan

Do you see it as perhaps some sort of complexing thing? And if so, have you considered using other things, like crown ethers?

Answer: Ian MacLeod

One of the things that we want to do is try and take a sample of the iron-rich PEG-water mixtures and extract them and see if we can get characterization, and the speciation of the iron, i.e. what form does the iron have as it is coming out of that mixture? If you know that then you have the lead into understanding the mechanism since you know your mechanism you can then tailor-make your molecules to go in there and rip the iron out. If necessary you could have a two-stage treatment for an object; you have one stage of treating the composite object for removal of the iron and the chloride and then you move over to a treatment that will enhance the wood. Another point to note is that because of limited resources we have tended to leave objects in solution of long periods of time, it has meant that a lot of the chlorides have been extracted. We find that when we compare objects that have undergone shorter rather than longer *impregnation* periods that after three *years* we have more post conservation changes with the objects that did not undergo a longer impregnation period. I am talking about intimate mixtures of iron and wood that are stored without a humidity-controlled environment.

Question: Margaret Baron

Ian, does that mean that when you are initially receiving in an artefact, i.e. wood with impregnation of iron, that you would immediately place it into a 5% PBG solution rather than going through deionized water desalination stage?

Answer: Ian MacLeod

On the basis of what we have done; you bet. Because if we just compare the rate in distilled water, for the second phase of the experiment, it is around about 10 micrograms of chloride per cane per hr^{1/2}, and if you look at it in 5% it is about 5 to 6 times the deionized water rate. I think really that answers the question.

Question: Mike McCarthy

Ian, does that mean that you are going to put my engine in polyethylene glycol?

Answer: Ian MacLeod

No, no, not the engine because with the case of your engine we were successfully able to separate the wood components from the bulk of the iron. But it means that when we are

treating iron-impregnated timber attached to the bearers, we now know what solution to put it in to get the maximum extraction of the iron from it in the shortest treatment time.

Question: Donna Stevens

That would actually explain what happened when we had a degraded boat in water storage for quite a number of years and we just put it in a PEG tank at a very low PEG solution and the iron just flushes out on to the surface. That would actually explain it!

Answer: Ian MacLeod

Yes, and the lovely thing is that that scum that floats to the surface in 5% PEG solutions has been identified as lepidocrocite, one of the iron oxyhydroxides. The beauty of it is because it is voluminous it doesn't inhibit the rate of release of the iron and the chlorides into the solution because that is always one of the problems you think about; all this material is precipitating on the surface of my object, is it going to slow down the rate of release of the iron and the chloride already in there and the answer is that data shows no. That in itself is very good because it means that you don't have to go round every day or every week and scrub, scrub, scrub, because none of us have got the time or the resources to do that. You can stick it in there and walk away from it and forget about it. We haven't looked at any temperature effects. The ambient temperature was used in this case and that is $22\pm 1^{\circ}\text{C}$, so they are the conditions under which the experiment was carried out. I think your rates of removal would be increased with temperature. The problem of furnace maintenance and also the cost of fuel are factors to consider when deciding on a room temperature versus an elevated temperature treatment programme.

Question: Cliff McCawley

Would this idea of using 5% PEG apply to sulphides?

Answer: Ian MacLeod

I do not think so.

Question: Cliff McCawley

I remember that when I was in Edinburgh that the same kind of observation was made, that PEG did bring out iron and did bring out chloride. When we were talking about heavily waterlogged oak, heavy with sulphides as well, there didn't seem to be any.

Answer: Ian MacLeod

No, it is the difference in the whole business of the solubility and the inherent chemical reactivity of the two forms of the iron and that is why I think it is so important when you are dealing with your archaeological objects to carry out your mineralisation and other analyses so that you know what form the iron is there you can have a much better idea of how you can optimise your conditions for getting it out. Of course the problem with iron sulphides is that anything that will take out iron sulphides will destroy your object. You can use cyanide solutions to dissolve sulphides but a lot of people get a bit twitchy about it. I am not a wood chemist so I don't know what effects cyanide would have on wood structure, but I think 10% cyanide solutions wouldn't be too good on wood.

In simple terms, for iron sulphides I don't have any answers. With the *Batavia* timbers you will see, on the curved part up near the mezzanine floor, that it is all rusty. Because iron sulphides were in the timber and the treated timbers were stored at too high a relative humidity, they oxidized up and then we have had to deal with the problem after that.

Question: Wal Ambrose

The question of raising your temperature of your bath to lure out the chlorides and iron; usually if it is a diffusion system, like you've got here, you get a logarithmic relation with temperature so that you only need a small rise in temperature to enhance the rate.

Answer: Ian MacLeod

Being honest, I didn't know these results were going to work out like this in the final form, until approximately one week ago and so therefore we haven't been able to *carry* out those experiments, but I think it will be really worthwhile to do. One of the advantages in Western Australia is that when we are treating iron objects, we have black bubble plastic blankets to cut down evaporation, and of course the water gets quite nice and warm, and the diffusion rates move up. The *Xantho* tank one summers day was 32°C. That is an advantage for those who are in sunny climes and even if you are not, just the fact of providing some form of insulation can really make a lot of difference to the rate of some of your processes.

Question: Wal Ambrose

The slide where you have great elbows in the curves, can you explain again what you think the reason for that is? Is it to do with concentration gradients within the matrix?

Answer: Ian MacLeod

It is partly to do with concentration but you've got a very complex system and you are looking at the inward diffusion of your solvent mixture. Because of the concentration gradient depends on the ratios across that diffusion barrier you would inherently think that increasing the concentration of your solvent system is going to improve you rate. However, you have got the counteracting effect of the change in the viscosity, which increases with concentration and has a slowing effect of the inward migration of the PEG. My feeling is that the first stage relates to the removal of iron and chloride from the concretion that had been affected by the previous work environment of sitting in the treatment tank, for 18 months, so in the first couple of months of treatment you were seeing that the interaction of the PEG with the previously modified nature of the concretion. After that time that PEG solvent mixture had got in beyond the affect of the previous environment and was then into fresh concretion. For a freshly excavated object you would start from that point. These two stages in the rates are due to the fact that I didn't think of the experiment until we had the object in our hands and by that stage it had been electrolysed for eighteen months.