Conservation of Waterlogged Archaeological Wood

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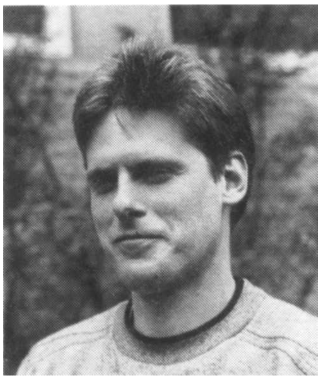
1 Introduction

Artefacts made from organic materials as a group present severe conservation problems. Of the organics, wood is perhaps the most important. It certainly constitutes the bulk of material excavated. As it was used by everybody in early societies, from cradle to coffin, its study can help improve our understanding of those societies.

The use and conservation of wood is complicated by the fact that it is not an engineered material, like metals or plastics, but is 'designed' to support the photosynthetic apparatus of a tree, and to transmit materials between its leaves and roots. Reflecting these requirements, and the biological growth and development of the organism itself, its structure is complex, as shown in Figure 1. This figure shows a highly idealized structure. In fact, no two trees are identical, and neither is the wood from them. Species is important, and this will influence the distribution and nature of the chemical components, which will change the rate and nature of the decomposition process at a molecular level. Added to this, knots and grain directions influence the mechanical behaviour and permeability of the wood which further complicates the pattern of deterioration.

Wood's structure is based upon the controlled use of two biopolymers, cellulose and lignin (Figure 2). Whilst cellulose has a high tensile strength, the presence of lignin in the cell wall increases its resistance to compression. Polyoses, polymers of sugars and related monomers, are the third major constituent. These usually exhibit complex chain branching patterns, and are less crystalline than cellulose.[1] The mechanical role of polyoses is not well understood, but they do form hydrogen bonded complexes with cellulose, and covalent bonds to lignin. Polyose association with these materials, and its high concentration in the cell wall, indicate that it too performs an important mechanical function, probably in transferring stresses between the other components, by acting as an adhesive. Similar materials used in modern composites include unsaturated silicone oils, used to coat glass fibres prior to impregnation with resin in the formation of fibreglass. These improve the wetting of the glass with the resin, and increase the bonding between the two components, so improving the mechanical strength and durability of the composite.



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2 The Deposition Environment

The deterioration of artefacts made from inorganic materials in a given deposition environment is fairly readily understood in terms of simple chemical redox equilibria. The decay of organic materials is governed by the same thermodynamic principles, but the reactions are usually mediated by living organisms,[4] some of which are listed in Table 1. This makes the decay process very dependent upon the chemistry of the deposition environment.

Artefacts made from organic materials, including wood, are only preserved in two specific types of deposition environment. The first is where the artefact is kept dry, and the other is by the development of an anoxic environment about the artefact. Although desiccation is an important preservation environment, as in Egyptian tomb finds, a lot of archaeology must rely upon organic material entering an anoxic state to be preserved. This can occur in waterlogged sites, in which organisms use up the oxygen about the artefact. If the diffusion path for more oxygen entering the deposition environment is long enough, then most biological activity will cease. Biological attack will, however, recommence as soon as the sample's environment will allow it. Display in a museum will not prevent further attack, and consideration should be given to minimize this possibility as part of the conservation process.

2.1 Biological Decay Processes

Seasoned wood contains very little organic nitrogen, and is a poor food source as a result. It can, however, be eaten by bacteria and fungi. The polyoses are the most easily digested components of the cell walls, but there is a slower loss of cellulose. Lignin is very resistant to biological attack, and, importantly, confers increased resistance to the other components in the cell wall. Although they do require the wood to be at least damp, fungi and bacteria are quite robust organisms, some bacteria can continue functioning in anaerobic environments. Under these conditions they use the iron(III) to iron(II), and the sulfate to sulfide redox couples to drive the digestion process. As a result of colonization by these organisms the amount of organic nitrogen in the wood is increased, and a wider range of organisms can eat it.

The result of microbial decay is a progressive weakening of the wood due to the sequential loss of these structurally important polymers. As material is lost, then blocks of sound material can become disconnected and so be unable to provide useful macroscopic support. Most wood types appear to deteriorate almost uniformly through their entire thickness. Oak, however, deteriorates slowly, possibly due to the presence of tannic acid acting as a biocide, or because of the low permeability of the material resulting from mineral inclusion. The pattern of deterioration is also anomalous, being characterized by a heavily degraded surface layer surrounding a core which is sound. These important differences in decay pattern are reflected in the classification scheme, originally developed by Christensen.[5] This scheme gives a simple description of the degree of physical deterioration of a wood sample in terms of the loss of solid components. The most heavily degraded wood is considered to be in class I, and the least degraded in class III, as shown in Figure 3. Surprisingly, it is in the soundest timbers, *i.e.* class III oak, where some of the biggest conservation problems occur.

Higher organisms can use wood either as a habitat or a food

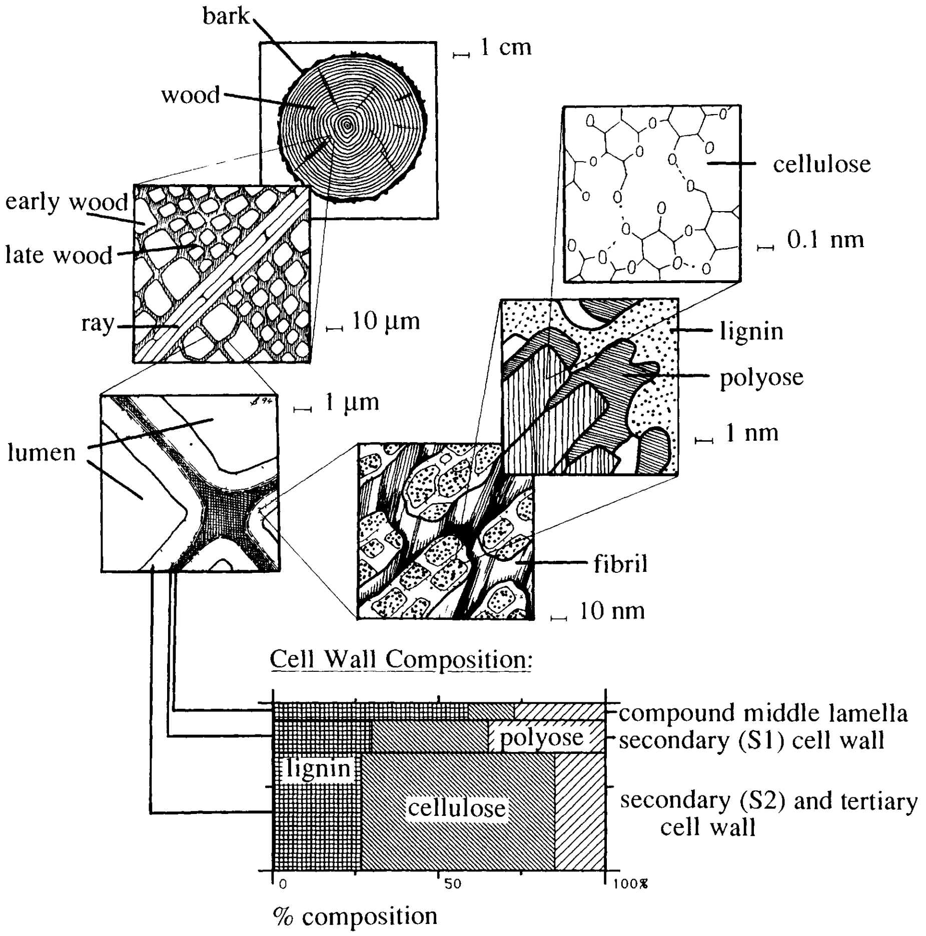


Figure 1 Wood, showing the interrelationship between materials and structures at a range of levels, from the molecular to the macroscopic. The section at 0.1 nm scale has been rotated through 90° to give a more standard representation of the cellulose molecules, in the other sections the cellulose molecules are ordered such that the chain direction is out of the plane of the page. Data from references 1 and 3.

source, and in the process of burrowing into its structure, they cause considerable macroscopic damage. In the marine environment crustacea, such as Limnoriidae (gribbles), and molluscs, such as Teredinidae (shipworms), are the principal agents of attack. Their counterparts on land are various insects. All of the higher organisms require oxygen, and some of them can survive in quite dry environments (termites are a good example, though they are not a problem in most of Europe), see Table 1.

2.2 Chemical and Physical Processes

Chemical hydrolysis can cause loss of polyoses and cellulose, though this route is not considered significant in comparison to biological attack. The fastest occurring chemical process is that of solvent swelling, where the cellulose molecules become surrounded by a sheath of hydrogen-bonded water molecules. This results in an increase in size of about 5% radially, 12% tangentially, and 2% longitudinally, and poses problems if fine measurements are required – for example, if medieval clog sizes were to be used to estimate the sizes of feet in the population.

Chemical changes also occur as a result of mineral inclusion. Sea salt is passively introduced in marine environments, but some ions, notably iron(III) are actively chelated by cellulose and tannates, and high concentrations of iron corrosion products build up in consequence. As the wood becomes anoxic, these salts are converted into sulfides. A physical consequence of mineral inclusion is that pores between lumina are blocked, and the wood can become impermeable. Other important physical processes are abrasion and compression of the material, which can make it difficult to judge its original form.

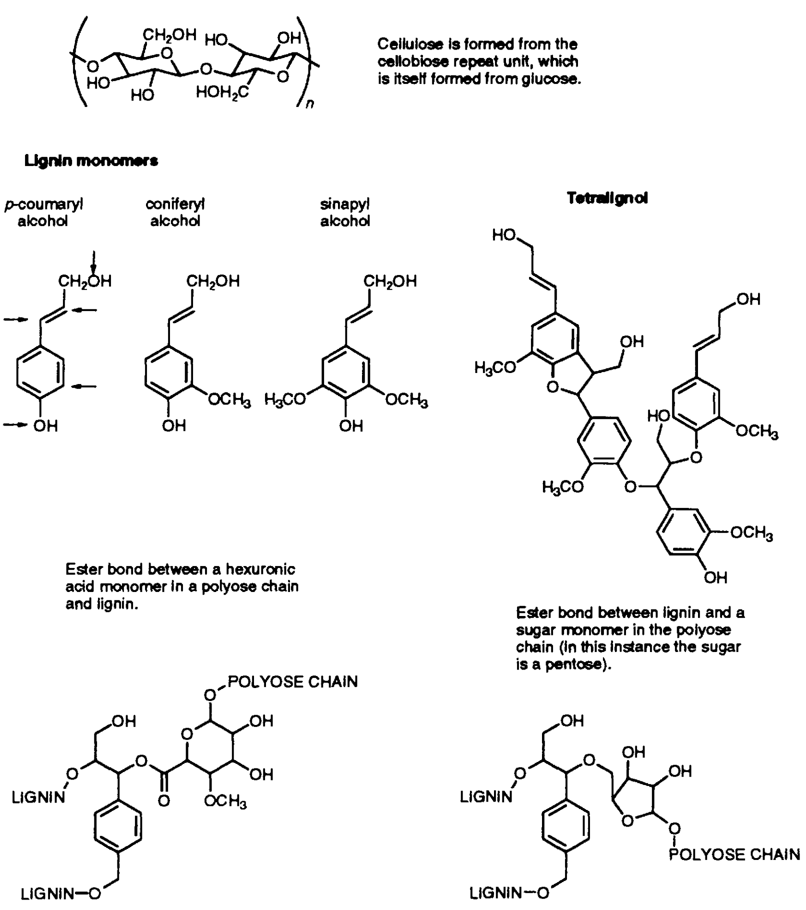
3 The Conservation Problem

Wood samples to be conserved are usually physically weak, due to decay processes, highly porous (though not necessarily permeable), and chemically very complex. The conservators job is to stabilize the sample, to give a permanent record, and to make the artefact suitable for display. Ideally the process should be quick, cheap, and robust, in order to cope with the large amounts of waterlogged wood which are excavated. In practice such a technique does not exist – commonly used methods can take 30 years to complete! As a result the conservation process is too expensive for consideration under any but the most important circumstances. A lot of material is, therefore, destroyed after excavation, and what is conserved tends to be part of 'one off', high profile projects.

The most active phase of a conservation treatment is in controlling the processes occurring as the artefact is transferred from its deposition to its display environment. Normally, one of the first steps must be to remove or pacify contaminants which will be unstable in the new environment and damage the wood's structure. Two important contaminants in this regard are sea salt and iron sulfide. If sea salt is present as the wood dries, then it will crystallize and damage the structure, as well as increase the artefact's tendency to absorb water and promote corrosion. Iron sulfide is unstable in aerobic environments, and its oxidation can destroy the artefact.

4 Chemical Stabilization

There are two chemical sources of conservation problems. First, the modification of artefact components through prolonged



Cellulose is formed from the cellobiose repeat unit, which is itself formed from glucose.

Lignin monomers

Tetralignol

Ester bond between a hexuronic acid monomer in a polyose chain and lignin.

Ester bond between lignin and a sugar monomer in the polyose chain (in this instance the sugar is a pentose).

Figure 2 The chemical structure of the mechanically important polymers in wood. The lignin precursors are biosynthesized from glucose, *via* shikimik acid.[1] Formation of lignin occurs by dehydrogenative polymerization at one or more sites (arrowed in *p*-coumaryl alcohol) to give a highly cross-linked polymer. The principal bonding possibilities are shown for coniferyl alcohol in the formation of tetralignol. The major mechanical role for polyoses is probably as an adhesive between the lignin and cellulose, whilst its close chemical similarity to cellulose allows the formation of hydrogen-bonded networks; bonding to lignin is achieved through ester or ether linkages.

Table 1 Decomposition agents for wood

Organism	Limiting Factor	Result
Bacteria	Require a wet environment	Loss of cell wall material
Fungi (moulds and rots) wide range of types: wet, dry, brown, and soft rots	Require O_2, and a wood moisture content (MC) of $> 18\%$	Loss of material and discoloration. Leads to massive loss of strength and slow disintegration
Insects, main European types include *Anobium punctatum* (woodworm) *Hylotrupes bajulus* (house longhorn beetle), and *Lyctus brunneus* (powder post beetle)	Require O_2, can survive down to 8% MC	Holes and cavities, rapid disintegration
Crustacea, eg. Gribble (*Limnoria lignorum*)	Marine environment, require O_2	Extensive galleries close to the wood's surface, and largely confined to the soft early wood
Molluscs *e.g. Teredo navalis*	as above	Small puncture holes leading to wide galleries and Swiss cheese interior

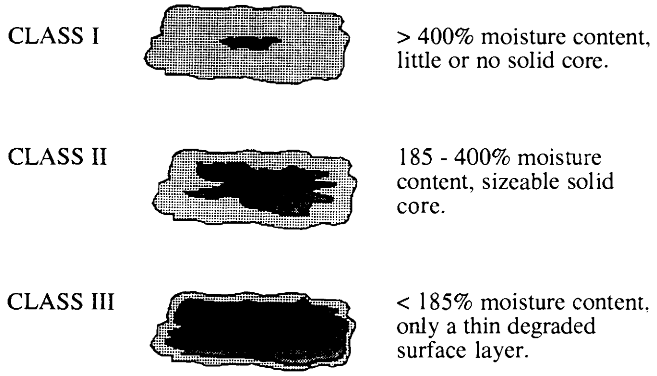


Figure 3 Classification of waterlogged wood in terms of its moisture content (MC). This is calculated as the weight of water divided by the dry weight of the wood. Modern woods have MC's of about 120% when fully waterlogged; higher values for timber of the same species therefore reflect the loss of solid material from the wood.

exposure to the burial environment. Secondly, the contamination of the artefact by minerals from this environment. The first problem is probably irreversible, involving loss of materials, random polymer chain scissions, and the first steps in the reduction of the wood to coal. By contrast, some chemical contaminants can and must be dealt with. As a consequence of the presence of high concentrations of iron pyrites in 'conserved' timber from the *Batavia*,[6] emergency conservation procedures have had to be adopted as a result of the oxidation reactions

Plate 1 Occasionally waterlogged wood can be air dried without the use of consolidants, as is the case with this long bow from the Tudor warship *Mary Rose*, which sank in 1545
(© The Mary Rose Trust, by permission)

Plate 2 This linstock from the *Mary Rose* demonstrates the most commonly used conservation technique for small artefacts, namely freeze drying after impregnation with PEG
(© The Mary Rose Trust, by permission)

Plate 3 A technique finding increasing favour amongst conservators is impregnation with sugars This can give a light, natural appearance to conserved wood, without the greasy texture sometimes evident on artefacts conserved using PEG This is demonstrated here by the use of mannitol on another linstock from the *Mary Rose*
(© The Mary Rose Trust, by permission)

Plate 4 Treatments using PEG and sugars are unsuitable for wood/iron composite artefacts These knife handles are from the Elizabethan warship *Makeshift*, which sank in 1592, and have been conserved by the author, using the supercritical drying technique The remains of the iron blade can be seen projecting from the handle in the centre

shown in equations 1 and 2. The initial oxidation half-reaction of iron pyrites is driven by the reduction of oxygen.[7]

$$FeS_2 + 8H_2O = Fe^{3+} + 2SO_4^{2-} + 16H^+ + 15e \qquad (1)$$

Once ferric iron is present, this can also oxidize iron pyrites[7] to give iron(II) sulfate tetra- and pentahydrates, products observable as a crystalline encrustation on timbers from the *Batavia*.[6]

$$FeS_2 + 7Fe_2(SO_4)_3 + 8H_2O = 15FeSO_4 + 8H_2SO_4 \qquad (2)$$

As iron(II) sulfate has less than half the density of iron pyrites, the resulting expansion results in structural damage, and blooms of sulfate crystals on the artefact's surface. In addition, the sulfuric acid produced starts to hydrolize the wood. The treatment adopted for the *Batavia* was to use ammonia gas to neutralize the sulfuric acid, and then to reduce the relative humidity about the displayed items, so as to reduce the rate of further oxidation.[6]

Ideally, iron pyrites should be removed while the artefact is still wet. The standard treatment is to soak in dilute hydrochloric acid, but a range of chelating agents have also been tried. The problem is that these treatments (particularly that with hydrochloric acid) result in some softening of the wood, and so are generally only applied to improve the appearance of the wood and not to reduce the concentrations of iron pyrites to 'safe' levels. Poly(ethyleneglycol), a commonly used consolidant, has been reported to reduce the amount of iron in treated timbers, but its effectiveness has never been convincingly demonstrated. (The *Batavia* had been treated with this material.) Perhaps the best method for protecting wood that is contaminated with iron pyrites is to keep the artefacts dry after conservation (see equations[1]).

By contrast with the problems caused by pyrites, sea salt is readily and cheaply removed by prolonged soaking in fresh water.

5 Drying Waterlogged Wood

Having chemically stabilized the wood, the second, and most expensive phase, is to stabilize its physical form as it is dried out. This drying process is similar in concept to seasoning fresh wood but whilst modern woods shrink, and can warp and crack during seasoning, it is normal for archaeological woods to suffer extreme distortion, and common for them to disintegrate.[9] As the results of failure here are catastrophic and immediately evident, most conservation research has been directed to solving this problem.

The principal forces acting on a material which is being dried are due to surface hydration energy and capillarity.[10] As it dries the water level recedes into the bulk of the material, and both forces act to draw the liquid out of the wet core into the dry surface layer. As a result the core is compressed, and the surface is placed into a state of tension. By allowing free movement of liquid, highly permeable materials suffer less drying stresses, as the hydrostatic forces are spread over a larger volume of the sample. All of the forces acting are transmitted to the solid matrix.

In wood, the situation is complicated by the distribution of pore sizes, as demonstrated in Figure 4, and the wide variation in permeability possible in any sample. Class III timber is difficult to conserve as the surface layer, which is most important archaeologically, is not strong enough to withstand the tensile forces exerted. These forces are exacerbated by the high strength and low permeability of the core of the timer.[11]

5.1 Avoiding the Formation of an Air–Liquid Interface

As a result of the forces generated during the drying process, considerable damage can occur to the wood. Possibly the most important job of the conservator is to ensure that this does not happen. The most elegant methods for doing this involve avoiding the formation of a gas–liquid interface during the process, and hence eliminating capillary forces. From the simplified phase diagram in Figure 5 it is evident that there are certain physical conditions under which a gas–liquid interface cannot be formed. These are found in freeze drying and where the liquid phase is converted into a supercritical fluid (a high pressure gas). Both techniques can be used on any class of wood, but they use equipment which places limits on the size of the artefact which can be treated. As a result, the artefact may have to be dismantled or sawn up prior to treatment.

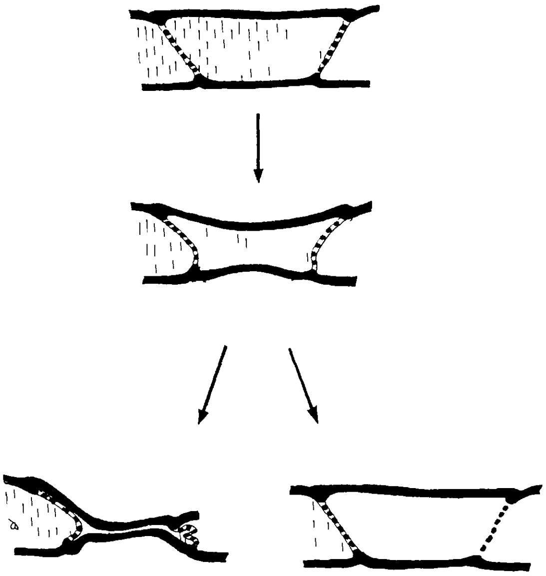


Figure 4 Surface tension holds the water meniscus at the fine pores between the cell lumen resulting in stresses in the cell walls which may result in physical collapse. If the tensile strength of the cell walls is greater than the capillary forces in the pores then the cell can recover its original shape.

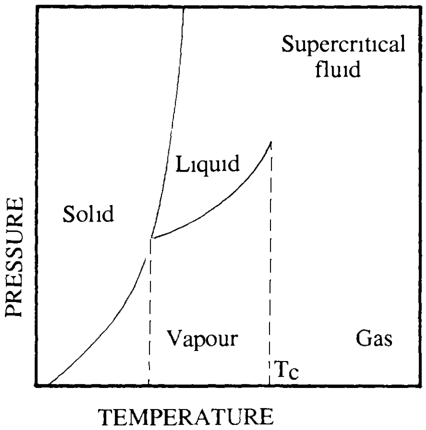


Figure 5 Stylized phase diagram. Only within the temperature region bounded by the critical temperature (T_c) and the triple point can a liquid phase be formed. To avoid drying stresses the vehicle must therefore be kept out of this region as it is removed from the wood.

5.1.1 Freeze Drying

In freeze drying, water vapour is sublimed from the sample, which is kept frozen during the process. The technique has a long pedigree, having been used as a method for preserving food by the Inuit (making 'klipfish') and by the Aztecs. Modern commercial equipment place the samples to be dried in vacuum chambers to increase the rate of evaporation, and hence the speed of the process.

The technique is not as straightforward as it might appear, as there is a considerable reduction in density as water freezes, and hence a physical expansion of the material within the sample. As a result, for freeze drying to be a useful technique for treating wood, a cryoprotectant must be added. The purpose of a cryoprotectant is to reduce the volume change by continuing to increase in density as the mixture cools through the water's freezing point. The most commonly used cryoprotectant is poly(ethylene glycol) (PEG), with an average molecular weight of 400 (usually referred to as 'PEG 400'). It is usual for waterlogged wood to be equilibrated with a 20% solution of PEG prior to commencing the freeze drying process. Often a high molecular weight grade of PEG will also be used, to provide support for the cell lumina after drying.[13]

The problem with the use of cryoprotectants is that they complicate the freezing process. It is frequently assumed that the mixture will freeze as a eutectic, in practice it is more normal for a glass to form. Whichever process occurs, the composition of the solid is not homogeneous, and sublimation will further adjust the relative amounts of the phases present.[15] Knowledge of the phases present, and their composition, is important in that some mixtures will not freeze. This is a problem with the commonly used mixtures of PEG 400 and PEG 3350, which do not freeze above − 20 °C at high PEG concentrations.

The technique is relatively quick, requiring about two years for the wood to take up the required cryoprotectants and consolidants, and a further two months for drying frozen under vacuum. Its major advantage over more traditional techniques is that it does not contaminate the sample with large amounts of consolidants, so the wood retains a fairly natural appearance. This is the method of choice for items small enough to be fitted into available freeze dryers, and has been used extensively on items recovered from the Mary Rose.[16] On the basis of time and cost, it is probable that the Dover Bronze Age Boat will be conserved by freeze drying.[17]

5.1.2 Supercritical Drying

The technique of supercritical drying (SCD) was invented in the 1930s by Kistler.[18] It allows gels and other low density materials to be dried from the liquid phase, in which they are prepared, without damaging their structure. We have recently extended this technique, as a series of experimental studies, to the problem of drying waterlogged archaeological wood.

SCD works by converting the liquid phase into a supercritical fluid. This is done by adjusting the temperature and pressure of the system until the densities of the liquid and gas phases become identical, at this point the interface between the phases vanishes. As long as the temperature is not allowed to fall below a certain critical point, then the supercritical fluid can be removed from the samples simply by reducing the pressure, without the formation of a liquid–gas interface at any point. In the absence of a liquid–gas interface, the stresses associated with surface tension forces are not developed within the sample. As it is these forces which lead to structural deformation and collapse, then no damage is caused during the drying process.

As wood polymers are damaged above 120 °C, water, which has a critical temperature of 374 °C, cannot be used. Other materials with suitable physical properties include chlorofluoro carbon compounds, hydrogen chloride, and sulfur dioxide, all of which are chemically or politically unsuitable, or xenon, which is very expensive. In practice, carbon dioxide is the most appropriate fluid to use on waterlogged wood. Unfortunately, as water is almost insoluble in supercritical carbon dioxide, it is necessary to exchange all of the water in the wood for methanol, prior to extraction with carbon dioxide in an autoclave.[19] Alternatively, a single exchange process can be carried out with an acetal or ketal (we use 2,2-dimethoxypropane) in methanolic solution. This allows rapid chemical conversion of the water present, as shown in equation 3. The dehydration reaction must be carried out in methanol to make the water and acetal miscible. H^+ is required as a catalyst, but protonated cation exchange resins can be used to prevent the artefact being contaminated or attacked.

$$\mathrm{CH_3C(OCH_3)_2CH_3 + H_2O \overset{[H^+]}{=} CH_3COCH_3 + 2CH_3OH} \tag{3}$$

The advantage of the technique is that it does not require the use of consolidants, and as a result the process can be completed within a few days. As yet, however, the technique has only been used at an experimental scale.

5.2 The Use of Consolidants

Whilst the preceding techniques are physically elegant, they are unsuitable for treating large items. Also, prior to the introduction of freeze drying, other methods had to be used to prevent damage to artefacts as they dried. These treatments rely upon strengthening the wood structure (to allow it to resist the forces exerted during drying) through the introduction of a consolidant into the cells. The treatment time is governed by the rate of diffusion of consolidant through the wood to where it is required, from a bath or spray arrangement which is continuously delivering consolidant in solution to the surface.

The earliest technique used on a large scale was to treat the samples by dipping in a hot, saturated solution of alum (potassium aluminium sulfate). This was very quick, and gave apparently good results, in that the wood surface usually retained its shape. By analogy with the earlier discussions on the drying process, it is evident that the alum operates by armouring the suface layer of the wood. The presence of alum increases the tendency of the treated surface to pull water out of the wet core, during drying, and so increase the compressive forces here, but the surface, which is largely solid alum, will not collapse.

The result is a surface layer, like an egg shell, within which is a cavity where the core has shrunk away, and finally, a very shrunken core. Clearly, such a sample is very weak, and subject to brittle fracture. An additional problem is that some of the alum re-enters solution, or recrystallizes, with every change in relative humidity, resulting in the formation of larger and larger crystals within the wood structure. The effect is that of a time bomb, the sample eventually completely disintegrating – and because of the internal damage to the wood structure, there is little possibility of being able to rescue the artefact. As a result, alum is no longer used, and considerable emphasis is placed on adopting techniques which are reversible.[5]

The principal cause of the problems with the alum treatment is that it only reinforces a thin surface layer of wood. Clearly, successful methods must treat the entire sample, but to do this it is evident that the chosen consolidant must be able to reach the core of the wood. Only low molecular weight materials diffuse rapidly, and some of the larger molecular weight materials may be incapable of entering the wood at all. This is a problem encountered with oak in class III, where it is difficult to penetrate the better preserved core wood with high molecular weight polymers. This problem has now been largely circumvented through a better understanding of the processes involved and the action of the materials used.[9]

Essentially there are two processes which can increase the strength of the wood.

Bulking. Material penetrates the micro-capillaries in the cell walls themselves, and provides additional strength to the existing structure. Clearly, from Figure 1, only small molecules will be able to penetrate the cell wall, and these must key into the residual chemical structure. This approach will work only if there is a significant amount of the cellulose remaining. The exact mode of action is unclear, but it is evident that the low Mr polymers used (*e.g.* PEG 400), which are liquids, do not provide strength directly. One possibility is that these materials act indirectly by reducing the vapour pressure of water present in the cell wall capillaries, and so retain water in this structure. This would help to keep the cell walls turgid, and so may provide hydraulic support as the lumen dry.

Impregnation. Here, large amounts of material are introduced into the lumen of the wood cells, this material acts directly to support the cell walls, and prevent their collapse As a result an impregnant must form a solid support as water is removed This usually means that high molecular weight impregnation agents must be used, and these cannot be introduced quickly or the wood will undergo osmotic collapse Consequently, methods that employ these agents can be very slow, and therefore expensive Also, the large amounts of material which must be introduced leave the polymer/wood composite looking waxy and wet – the result of the reduction in internal reflection of light from pores in the wood structure as cell lumen are filled

The most commonly used polymer, for both bulking and impregnation (using different average molecular weight grades), is poly(ethylene glycol) (PEG) Successful treatments of the Roskilde Fjord 'long boats' in Denmark have been carried out using PEG 3350 (earlier work[5] refers to this polymer as PEG 4000), and, more recently, the Yuan Dynasty Ship has been treated with the same single molecular weight grade of PEG [20] Unfortunately, class III timbers are not readily treated by either impregnation or bulking agents on their own, and combinations are most often utilized, as discussed below A major disadvantage with the use of PEG is that it is hygroscopic, and accelerates the corrosion of iron and other metals As a result it cannot be used to treat artefacts containing these materials Furthermore, treated objects must be kept in controlled environments to prevent PEG migration and loss from their surfaces

Water is the preferred vehicle for consolidants, but advantages can be obtained by the use of other solvents as many of the problems encountered result from the physical properties of water, such as its high surface tension A further advantage of using non-aqueous solvents is that they can be used to introduce hydrophobic consolidants These substances are unlikely to key into the cellulose structure, but can be used as impregnation agents, when they will tend to make the wood composite product a lot less likely to absorb water, and so be less susceptible to dimensional instability due to changes in relative humidity

The problem with non-aqueous solvents is that most are a fire and health risk, whilst all are comparatively expensive, and present disposal difficulties A few techniques have been used, the most effective of which are impregnation with rosin from acetone solution, and wax from toluene The acetone–rosin process can be used to treat iron composite artefacts, and does produce a durable, if brittle finish Unfortunately, the treatment is hazardous, as large amounts of infusion solution must be heated close to the boiling point of the acetone in the final stages of the treatment to get enough rosin in to stabilize the wood The reversibility of this treatment is questionable, and the loss of internal detail is sufficient to make dendrochronology impossible

5 2 1 Combination Treatments

These use a combination of bulking agent and impregnation agent in the same treatment, though not usually at the same time It has the advantage of allowing all timber types to be treated, but the treatment times can be very long

A method developed to treat the *Bremen Cog*[21] is to employ an initial treatment of PEG 400, followed by a separate treatment in which the concentration of PEG 3350 is slowly increased to the desired amount These treatments must be carried out separately, as a mixture of the two forms a sticky mess with no mechanical stability The intention of this treatment is, therefore, to bind the PEG 400 into the cell walls prior to addition of the PEG 3350 [It is not, however, apparent that this is the thermodynamically stable situation, and post-treatment desorbtion and dissolution processes do not appear to have been addressed] The *Wasa*, which started active conservation in 1962 (and is still being sprayed occasionally today) also used a range of molecular weight grades of PEG [22]

An example of a variant of this technique which is finding increasing favour, owing to its low cost, is the use of sugar (sucrose) [23] This can act as both an impregnation and a bulking agent, because of its small molecular size, high compatibility with cellulose, and good rigidity when dry Unfortunately its performance is variable, and there is some concern over its biological stability Anybody who has kept jam in an open container will be more than aware of the possible problems

5 2 2 In situ Polymerization

Owing to the difficulties in getting pre-formed polymers into the wood, considerable work has been carried out in an attempt to develop monomers which can be polymerized *in situ* after infusion The advantages to this are obvious, but work in this area has met with only limited success This is because the monomer chosen must not polymerize until the infusion process has been completed, otherwise the wood would become impermeable and the core remain untreated Even when using small molecules, treatment times of several months or years are likely, so the problem of monomer stability is not trivial Further problems are that the polymerization process is difficult to control within the wood, and that the process is irreversible Only two techniques are employed

The most common is the use of melamine formaldehyde resin (frequently referred to by the trade mark 'Lyofix') Since the monomers are infused in alkaline solution, complete treatment must be quick, to prevent hydrolysis of the wood The monomers are subsequently polymerized by the addition of acid Large items are not easily treated by this technique, and even small items may require multiple treatments to build up enough strength to survive drying

The second method is to use radiation curing to produce polymers Clearly this presupposes a high energy radiation facility, but it does allow more stable monomers to be used A wide range of polymers can be made by radiation curing, but only a few have been found to give acceptable results with waterlogged wood and these have all required the use of non-aqueous solvents as vehicles for the monomers Poly(methyl methacrylate) has been used fairly successfully, but the resin shrinks considerably during curing, and this can lead to extensive cracking More modern techniques employ unsaturated polyester oligomeric resins, which are linked by radiation curing of styrene, also present in the infusion solution (see Scheme 1) The product of these techniques is mechanically strong, durable, and stable to a wide range of environmental conditions Its utility in treating iron composites does not, however, appear to have been addressed This technique was developed in France, and has been used there on several sizeable projects [24]

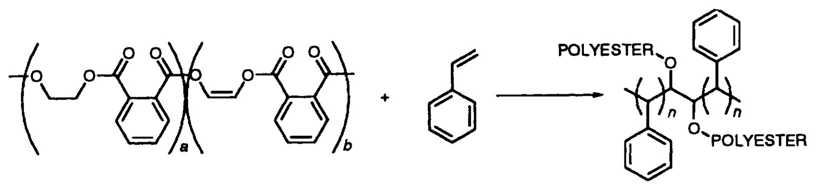
Finally, considerable work has been carried out on the formation of silica within wood, by treatment with alkoxy silanes in acetone solution, to form wood/ceramic composites Although these may be interesting from a materials perspective, they have found no favour amongst conservators Although the environmental stability is improved, the colour of treated material is poor, and the results are variable

6 Maintenance

It is normal to consider the conservation process to be over when the artefact moves into the storage or display environment after drying and stabilization by the preceding techniques It is, however, more accurate to state that it simply moves into a new phase of the process Complete destruction of many collections has occurred through inappropriate, or non-existent curation Although the active conservation phase is expensive, the cost of the obligation to indefinite maintenance must be considered

This clearly places an obligation upon the conservator to minimize the subsequent costs of maintenance if this is possible without unnecessary risk to the artefact Whilst the curation phase is really beyond the scope of this article, it is evident that the choice of technique used to stabilize waterlogged artefacts will greatly influence the subsequent ease of their maintenance

In addition to the factors already considered, the facility with which treated items can be repaired if damaged,[25] and the compatibility, or requirement, of the treated wood for barrier



Scheme 1 An unsaturated isophthalic polyester, can be cross-linked *in situ* in wood by radiation-induced curing of styrene, to give a strong composite material, with good environmental stability

coatings (varnishes *etc*) should be assessed [26] Only the radiation-cured monomer technique gives material stable enough for general display purposes, the techniques in common use require purpose-built facilities to ensure a suitable environment for the conserved artefact As a result, factors such as light intensity, air-borne pollutants, heat and humidity regulation are a function of the display engineering [27] The environmental stability of supercritically dried wood is still under investigation

7 Conclusions

The importance of wood as an archaeological material is in the evaluation of its usage, and as an aid to dating both the artefact itself, and associated materials Any given artefact is liable to be interpreted several times by different workers in different fields, and so as much of the information content of the artefact must be preserved as possible For example, a boat find will be examined and identified by the excavator, the excavator's plans will then move on to a ship designer to obtain a reconstruction, probably in the form of a computer CAD file This might move on further to tank tests on a physical model Attempts would be made to analyse the wood surface, to obtain evidence of the use of anti-foulants, paint, and tool marks From this information it may be possible to determine the way, and with what tools, the boat was built Finally, analysis of the associated flora and fauna might tell where the vessel has been, as differences in species and biological form are observed between temperate and tropical waters From these pieces of information a considerable amount of evidence can be built up about the society which used the vessel, their technical competence, mobility, and aesthetic values With this understanding, and by correlation with other work, it is possible to build up an accurate picture of what was actually happening in a society

The process of obtaining information from an artefact, and the dissemination of that information, is a long term project There is also a duty to inform and educate, and this means displaying the object, and explaining its relevance to the general public effectively Ideally, the conservation process should stabilize the artefact without damaging any of the information associated with it It is evident that in the past conservation treatments have not guaranteed an artefact's stability, and perhaps even today we should give more consideration to the likely 'shelf life' of conserved artefacts The main techniques in use today are freeze drying, and combination PEG treatments, though there is considerable interest in the use of sugars These methods, which attempt to preserve the entire fabric of the artefact, are an improvement on the old alum treatment, in that they offer the possibility of reversal if this became essential It is evident, however, that our understanding of some of the basic thermodynamics and kinetics pertaining to the components of the wood itself, and to their interactions with the consolidants in use, is limited Not only, therefore, is there a requirement for improved treatments (to cope with composite artefacts, for instance), but there are still important questions to be answered about the long term consequences of many of the procedures in use today

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8 Bibliography

The problems with the conservation of waterlogged wood have been subject to numerous international working group meetings under the auspices of the International Council of Museums (for example, references 6 and 12) Whilst published proceedings of these meetings monitor the pulse of the discipline, a more readily available review on all aspects of wood conservation is 'Archaeological Wood' by Rowell and Barbour [2] Earlier work, much of it seminal to the modern development of the field, is given in a personal account by Christensen [5] The reader interested in a modern comprehensive text covering a broad range of artefacts and materials recovered from the marine environment will find Pearson[8] an approachable, if expensive, text The conservation and deterioration of synthetic and natural polymers other than wood is addressed in 'Polymers in Conservation' [26]

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