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# Conservation of Waterlogged Wood—Past, Present and Future Perspectives

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**Abstract:** This paper reviews the degradation, preservation and conservation of waterlogged archaeological wood. Degradation due to bacteria in anoxic and soft-rot fungi and bacteria in oxic waterlogged conditions is discussed with consideration of the effect on the chemical composition of wood, as well as the deposition of sulphur and iron within the structure. The effects on physical properties are also considered. The paper then discusses the role of consolidants in preserving waterlogged archaeological wood after it is excavated as well as issues to be considered when reburial is used as a means of preservation. The use of alum and polyethylene glycol (PEG) as consolidants is presented along with various case studies with particular emphasis on marine artefacts. The properties of consolidated wood are examined, especially with respect to the degradation of the wood post-conservation. Different consolidants are reviewed along with their use and properties. The merits and risks of reburial and in situ preservation are considered as an alternative to conservation.

**Keywords:** waterlogged wood; consolidation; archaeological wood; sorption; degradation; drying; wood conservation; PEG; alum; reburial; in situ preservation

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## 1. Introduction

Archaeological wood is defined as old wood that shows evidence of having been worked by humans, while "waterlogged" means that all the pore spaces, including capillaries and microcapillaries, are entirely filled with water [1,2].

Wood is an important material that has been used for shelter, tools and weapons since the time of the earliest hominids. It is a composite material with a hierarchical structure that is primarily composed of three polymers: cellulose, hemicellulose and lignin. When a tree dies, the wood decays under conditions where there is sufficient water and oxygen to allow decay organisms to metabolise the chemical constituents, but in the absence of either component in the environment, fungal decay does not occur. In arid conditions, wooden objects from ancient Egypt have been preserved for 5000 years, and under waterlogged conditions, where there is limited oxygen access, it is possible that wood can survive for a considerable period of time. The Shigir Idol, which was discovered in a peat bog in the Sverdlovsk region of the Urals, has been dated to the late Younger Dryas, about 12,000 years ago [3], although this age is insignificant compared with the Schöningen spears, which are over 300,000 years old [4]. Whereas no wood was recovered from the Sutton Hoo ship burial, which was located in sandy soil with good air permeability, wooden objects from the Oseberg and Gokstad ship burials, located in waterlogged environments, were extremely well preserved [5,6].

Although the appearance and structure of waterlogged wooden artefacts may be preserved, the wood is still degraded. Water-logging and anoxic conditions prevent fungal metabolism, but bacterial attack and chemical degradation can still occur, leading to a loss of strength and structural integrity of the object. As a consequence, it is necessary to undertake some sort of conservation measures to preserve the wood, to prevent collapse during drying and maintain some mechanical strength, but many of these consolidation methods have subsequently resulted in problems that were not foreseen. In the past, alum was used as a consolidant, but there are now problems of extreme degradation of the wood. Polyethylene glycol (PEG) has often been used as the consolidant of choice because it is relatively inexpensive, stable and reversible. However, it produces objects that are heavy, with a dark and waxy appearance and is corrosive to metal [7].

The 1992 Valletta Treaty obliges signatory countries to protect their buried archaeological heritage, in situ, if possible. Where this is not possible, rescue excavation has to be undertaken with the remains protected from degradation. When archaeologically important sites are discovered, it is important to know whether the sites have favourable or unfavourable conditions for the preservation of remains. Based on this knowledge, it is then possible to determine the best strategy for the preservation of the artefacts. Although site reburial is one strategy for the preservation of archaeological remains, this can involve risks because the waterlogged conditions that resulted in the original preservation of the wood may not continue into the future [8–10]. Defining the characteristics of burial sites and their suitability for the ongoing preservation of their remains is a problem [11]. The most common parameters used to characterise sites are pH, redox potential (Eh), dissolved oxygen content, and the presence of ions, such as ammonium and nitrate. Depending on the dissolved oxygen content, the sites can be classified as anoxic, suboxic, dysoxic, or oxic. It is reported that oxygen levels of less than 0.3 $\mathrm{mL\ L^{-1}}$ prevent fungal growth, and environments are often characterised as being oxic or anoxic based upon the presence or absence of soft-rot fungi [8].

Consolidants for protecting waterlogged archaeological wood are available, but they all have disadvantages; is there one available that has optimal properties, or is more research needed to find the perfect material? Conservation agents for waterlogged wood should primarily provide integrity and dimensional stabilisation upon drying. They should also prevent further dimensional changes of the object, maintain, or improve its mechanical strength, and protect it against biotic and abiotic degradation. Conservation agents should be chemically stable, resistant to ageing/weathering, compatible with wood structure, and preferably bio-friendly and cost-efficient. Conservation ethics also impose the desirability to allow for the reversibility of the applied treatment or the possibility of further re-conservation using different agents. Due to the nature of conservation work: preserving the dimensions and appearance of ancient artefacts and making their history accessible to the public, treatments must be "gentle" in order to inflict as little damage as possible to the objects themselves. This often means long timescales and processes governed, for example, by diffusion of chemical treatments into artefacts lasting for periods of up to a year for immersion of smaller objects in tanks or, as for the Mary Rose, a spraying programme lasting over twenty years [12].

## 2. Degradation of Waterlogged Wood

Several different abiotic and biotic factors, including UV radiation, temperature and humidity changes, wind, precipitation, fungi, bacteria and insects, affect wood in the natural surroundings causing its degradation. Despite the multiple causes of wood degradation, the main decay mechanisms are similar at a molecular level. They involve hydrolysis of acetal linkages in polysaccharides (cellulose and hemicelluloses) and various redox and radical reactions of carbon, ester and ether linkages in the aromatic structure of lignin. However, in waterlogged environments, the range of the degrading factors is highly restricted, which significantly slows the decay rate, thus allowing the wood to survive even hundreds and thousands of years.

### 2.1. Microbiological Attack

Waterlogged wooden artefacts are generally discovered buried in bottom sediments of water reservoirs, wet soil or peatlands. All these environments offer highly reduced oxygen conditions, insufficient for typical terrestrial wood degraders such as brown rot and white-rot fungi. Therefore, they enable the growth of a restricted range of microorganisms. In anoxic or nearly anoxic waterlogged conditions, biodeterioration of the wood is mainly bacterial, while more oxygenated environments additionally facilitate decay caused by soft-rot fungi [2,13–15].

Wood-degrading bacteria are categorised into erosion, tunnelling and cavitation bacteria, based on the micromorphological degradation pattern they produce (the bacterial types do not represent any form of taxonomic classification) [16–18]. The most common form of microbiological attack in anaerobic or nearly anaerobic waterlogged environments is by erosion bacteria (EB). Erosion bacteria are spherical or rod-shaped Gram-negative cells that lack flagella. They are associated with a thick, polysaccharide-derived, slime layer and are motile via gliding [18–21]. The colonisation of wood by EB takes place from the surface, with invasion occurring via rays and pits and through the cell lumina. There is also degradation of the margo of the pits of the cell walls, leading to an increase in permeability of the wood [22]. The EB start attacking from the cell lumen, align themselves with the microfibrils and begin digesting cellulose and hemicelluloses from the cell wall starting at the S3 layer, leaving characteristic grooves. Attack proceeds through the cellulose-rich S2 and then the S1 layer towards the middle lamella. It is accompanied by the production of amorphous mucilage, which can be further colonised by different types of scavenging bacteria [20,21,23]. Even at advanced stages of decay, when the secondary wall layers are entirely decomposed, the lignin-rich middle lamella appears to be unaffected (only some minor modifications in lignin occur [24]). The remaining porous waterlogged lignin-rich material can still support itself and exhibit traces of its original manufacture. However, it may be very soft and easily deformed and will collapse upon drying. Because the bacterial attack is associated with the polysaccharide content only, changes in mechanical properties can be correlated with the relative lignin content of the wood [20,21,23,25].

Erosion bacteria can tolerate both low-oxygen and near-anoxic conditions; therefore, they can even decompose wooden artefacts that are buried deep in sediments; however, the decay is more intense when more oxygen is available [21,26]. They are slow degraders, and even after years of burial, they can still be actively degrading the wood [27]. A characteristic feature of bacterial attack is the lack of homogeneity, with heavily degraded regions of wood surrounded by regions that are unaffected [28], as well as variation in the extent of degradation of the different cell wall layers (Figures 1 and 2) [29]. The outer regions of the wood are usually characteristically more heavily degraded compared with the interior, which may remain relatively intact [30,31]. The extent of degradation is dependent upon timber species, dimensions, and whether the site is in marine or freshwater conditions [25], but is not necessarily related to the time of burial [2,13,32], and the role of nutrient enrichment on bacterial activity is poorly understood [19,33]. It seems that water flow stimulates EB degradation activity, which results from the low availability of nutrients in the surrounding area [26]. Interestingly, compression wood of pine apparently shows different degradation characteristics depending on the amount and severity of compression wood present, when compared to normal wood of the same species. In particular, severe compression wood showed a high degree of resistance of the outer S2 layer to bacterial erosion [34].

**Figure 1.** Slice of medieval waterlogged oak excavated from the Lednica Lake, in the Wielkopolska region, Poland, with a severely degraded, soft and light outer ring of sapwood (the loss of wood substance of about 70–80%) and a better-preserved, hard and much darker central part of heartwood (the loss of wood substance of about 10–20%) [35].

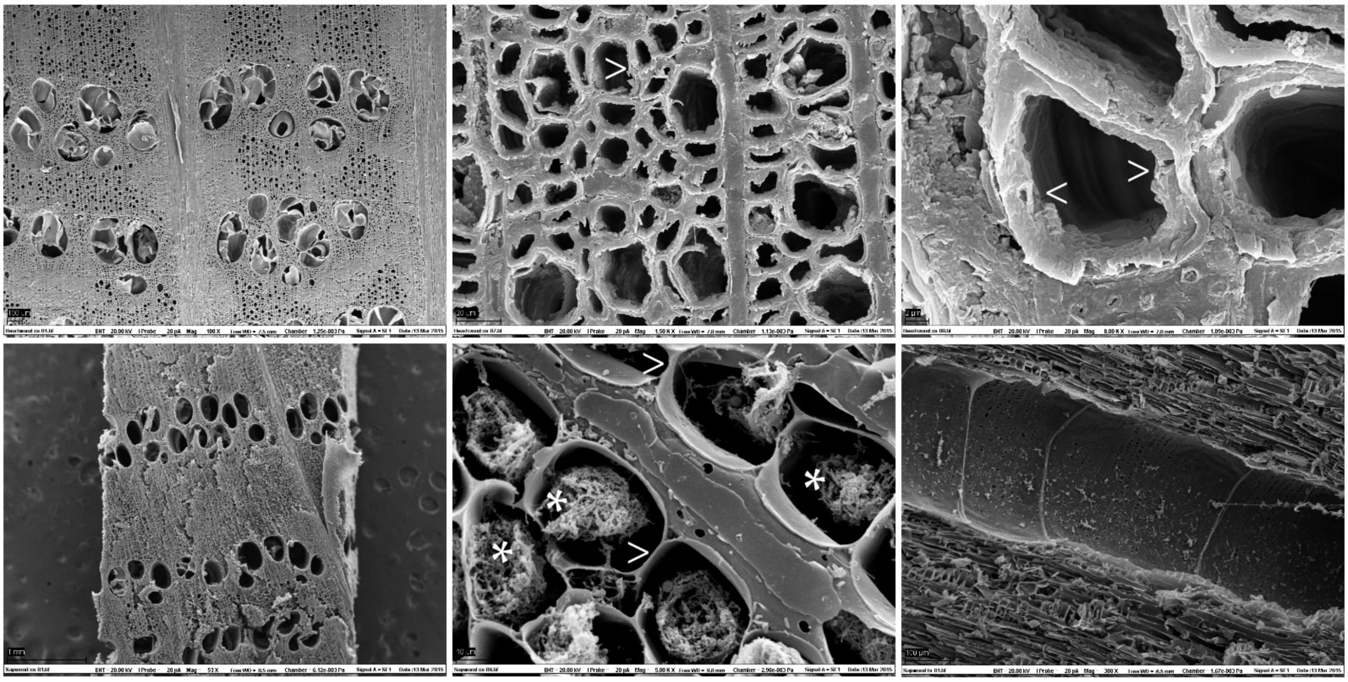

**Figure 2.** SEM images (Carl Zeiss AG-EVO® 50 scanning electron microscope using a cryo-SEM technique) of waterlogged oak excavated from the Lednica Lake; upper row—better-preserved heartwood (loss of wood substance about 10–20%) with thick cell walls (arrows) still consisting of all their layers (however sometimes partially degraded or detached); lower row—highly degraded sapwood (loss of wood substance about 70–80%) with a residue of the degraded secondary cell walls visible inside cell lumina (asterisks) and much thinner cell walls consisting mainly of the middle lamella (arrows).

Although degradation by erosion bacteria has been known since the 1980s, the bacteria responsible have not been isolated. Consequently, little is known about the conditions under which such organisms are most active. Culturing bacteria experiments and molecular DNA techniques have shown that bacteria in waterlogged wood belong to the *Cytophaga-*

*Flavobacterium-Bacteroides* complex, *Pseudomonas*, *Cellvibrio*, and *Brevundimonas* groups [36]. It was impossible to reproduce the decay patterns by monocultures in the laboratory, only by mixed cultures, which suggests that EB are active only when they form a synergistic, site-specific consortium with other degradative bacteria. However, they seem to be responsible for the initial attack of water-logged wood in anoxic or near-anoxic conditions [16,37,38]. Other opportunistic organisms, such as scavenging bacteria then begin to colonise and metabolise degraded polysaccharide material in the environment surrounding the erosion bacteria.

In conditions where there is some oxygen present, tunnelling and cavitation bacteria may also be responsible for wood degradation, and they often share this habitat with soft-rot fungi [13,20,21]. Tunnelling bacteria (TB) are unicellular, non-flagellated, motile, Gram-negative, spherical or rod-shaped bacteria. They can endure in a wide range of temperature and humidity conditions and are ubiquitous throughout terrestrial and aquatic environments. In nature, they often coexist with soft-rot fungi, degrading wooden substrates (of both coniferous and deciduous species) together [18,39,40]. Tunnelling bacteria colonise wood from the surface via nutrient-rich rays, and proceed through other lignified wood elements (tracheids, vessels and fibres) via pits or by direct cell wall penetration. TB adhere to the lumen side of the S3 layer using specific polysaccharides produced by themselves and then penetrate through the S2 and S1 layers towards the middle lamella, producing minute tunnels in different directions. They can degrade not only the polysaccharide fraction of the wood, but also the lignin-rich primary cell wall and middle lamella; however, much of the lignin still remains in the decomposed residual material. The ramified tunnels never cross each other, but when the wood is severely degraded, they may collapse, destroying the whole cell wall [17,24,39,40].

The third type of wood degrading bacteria are cavitation bacteria (CB). However, they are rarely reported and sometimes even considered a form of erosion bacteria under restricted conditions. Similarly to EB and TB, cavitation bacteria attach to the cell wall surface using polysaccharide slime. They pass through the small holes in the S3 layer towards the S2 and S1 cell walls, where they digest the polysaccharide fraction creating diamond-shaped or angular cavities. The middle lamella remains untouched. In contrast to EB and TB, degradation is localised mainly within the S2 layer and extends beyond the area where the bacteria are present. This suggests that cavitation bacteria produce diffusible enzymes which can penetrate the cell wall causing its degradation even at some distance from bacterial cells. The S3 layer usually remains undegraded or only slightly modified [16,17,20,24].

Wood from waterlogged sites, where some oxygen is available, shows evidence of soft-rot decay [14,18,25]. Soft-rot fungi belong to *Ascomycota* and *Fungi imperfecti* and are easily distinguishable from other wood-decaying fungi by the ability to degrade wood not only in terrestrial, but also in aquatic environments, and by the decay patterns they produce in wood. There are two decay patterns of soft-rot: type 1 and type 2. In type 1, common in gymnosperm woods, soft-rot produces specific spiral cavities within the S2 layer that follow the orientation of cellulose microfibrils. Depending on the wood anatomical orientation, the pattern can be seen as holes of different sizes (transverse sections) or long cavities with pointed ends (radial or tangential sections) in the secondary cell walls. At advanced decay stages, the entire secondary cell walls can be fully eroded, pointing at the ability of soft-rot to decompose all the cell wall components. However, lignin-reach cell structures or cell types (initial pit borders, middle lamella, ray tracheids of radiata pine) seem to be highly resistant to this type of decay. In type 2, typical for angiosperm woods, a diffuse form of cell wall degradation occurs. Fungal hyphae can colonise cell lumina and degrade the polysaccharide fraction of cell walls, leaving only lignin residues. However, in severely degraded wood, the whole secondary walls can be decomposed, leaving only relatively intact middle lamellae, which suggests that although soft-rot can easily metabolise cellulose and hemicelluloses, it is also able to modify lignin to some extent [14,39]. Sometimes also type 3 of soft-rot decay is described, when fungal hyphae actively penetrate cells and colonise wood tissue through a traverse perforation of adjacent cells [16].

Several freshwater (*Allescheria terrestris, Chaetomium thermophilum, Sporotrichum thermophilum, Thermoascus aurantiacus*) and marine species (*Ceriporiopsis halima, Humicola alopallonella, Lulworthia* spp., *Monodictys pelagica*) of soft-rot fungi have been described [18]. They can actively decay waterlogged wood in a broad pH range (3.7–8.6), but as sediments accumulate and cover wooden artefacts (or the decay reaches deep inside large wooden pieces) and the oxygen availability reduces, the soft-rot stops and wood degradation proceeds only by anaerobic or nearly anaerobic bacterial attack [18,21]. Different decay patterns observed in waterlogged wood tell the history of the object and its burial environment, e.g., evidence of the presence of tunnelling bacteria in the Uluburun ship suggests that the water was oxygenated enough to promote the growth of these types of microorganisms [17]. Usually, the outer parts are heavily decayed by soft-rot and tunnelling bacteria, while the inner regions mainly present the pattern of degradation by erosion bacteria that can survive in almost anoxic conditions [13,17,18,20]. Although it is commonly assumed that erosion bacteria are the only form of bacterial attack in anoxic conditions, this may not be entirely reliable since little is known about the influence of different environmental factors on bacterial activity [8], and the bacterial community may be composed of both aerobic and anaerobic bacteria [41].

The main problem resulting from microbial degradation of waterlogged wood is associated with the loss of wood strength. The excavated wood usually looks good (Figures 1 and 3A,B), although its outer layers may feel soft and spongy to the touch. The residual cell wall substances (in highly degraded wood mainly in the form of a lignin-rich skeleton of middle lamellae (Figure 2 lower row, Figure 4B1–B3) keeps the wood integrity as long as it remains waterlogged (Figure 3B). However, upon drying, the capillary forces of evaporating water may cause a collapse of the weakened and fragile cell walls, which leads to irreversible wood shrinkage and cracking (Figures 3C and 4B1–B3).

A wooden artefact destroyed this way loses its historical and aesthetic value. To prevent this, immediate conservation treatment is essential directly after excavation if the wood is intended to be saved in a dry state [13,15,21]. The choice of a proper conservation agent requires knowledge of both the alterations in the degraded wood and the phenomena that have resulted in these changes [21].

During excavation, storage and restoration, the wood may be exposed to oxygen, and fungal or bacterial decay may then occur (white-rot fungi can further degrade even heavily decayed artefacts deprived of most of the cell wall polysaccharides) [2,17,43–45]. The same may happen during excavation and reburial of the objects, when greater oxygen concentrations can reactivate the extant bacteria or support wood colonisation by a new population of microorganisms [17]. Microbial colonisation can also occur on the surface layers of archaeological wood during the treatment with PEG, sugars or other nutrient-rich compounds, which may affect the penetration of the conservation agent into the wood matrix but usually does not endanger the integrity of the treated artefact [43].

### *2.2. Waterlogged Wood, Sulphur and Iron*

In anoxic environments with low redox potentials, sulphate reducing bacteria (SRB) compete with other anaerobes, and in conditions of high sulphate concentration, SRB can outcompete such organisms, resulting in the enrichment of $H_2S$ in the local environment [46], which inhibits the activity of aerobic microorganisms. Where iron is present, the $H_2S$ reacts with $Fe^{2+}$ to produce iron sulphides, such as pyrite ($FeS_2$), mackinawite ($FeS$), or greigite ($Fe_3S_4$) [47]. Iron is a common contaminant in waterlogged wood, especially associated with shipwrecks, although iron concentrations in wood can vary considerably between and within sites [48].

**Figure 3.** Highly degraded waterlogged elm wood excavated from the Lednica Lake, the Wielkopolska region, Poland (the loss of wood substance was about 70–80% with highly reduced cellulose and hemicelluloses content [42]); (**A**) part of a log shortly after excavation (upper photo) and cutting (lower photo); (**B**) untreated waterlogged elm samples (completely filled with water); (**C**) untreated samples shrunken upon air-drying.

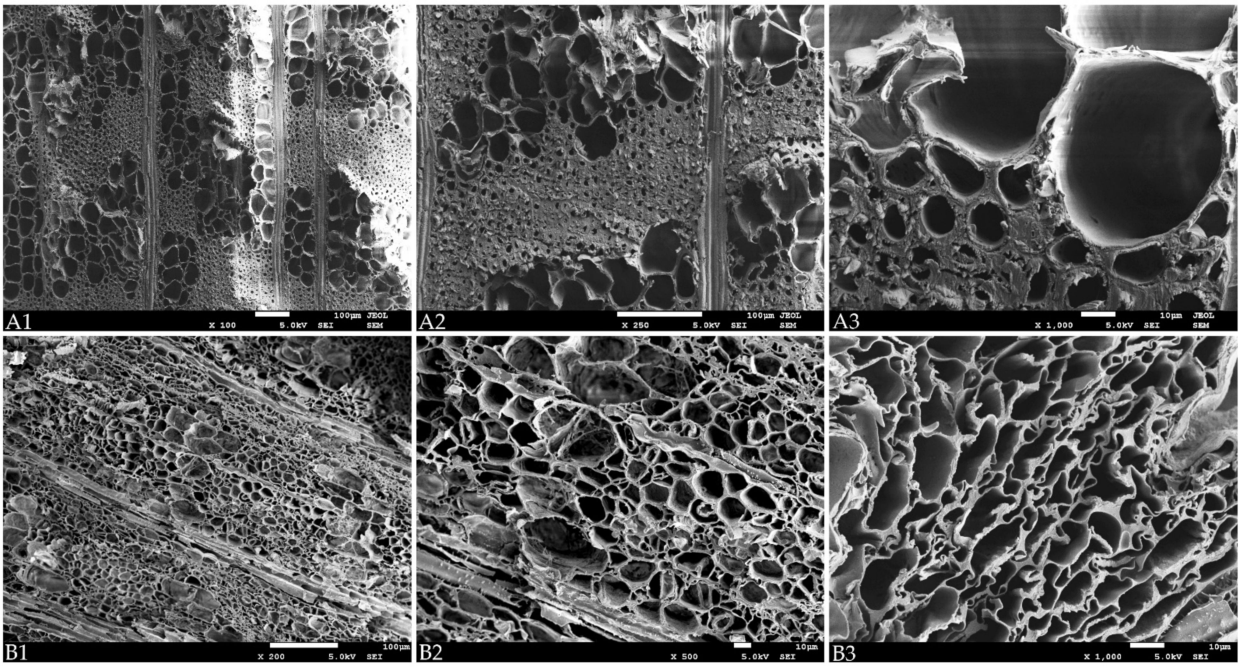

**Figure 4.** SEM (JEOL 7001F Scanning Electron Microscope (JEOL Ltd., Tokyo, Japan)) images of contemporary elm with undegraded thick cell walls (**A1**–**A3**) and heavily degraded waterlogged elm shrunken upon drying, with very thin and collapsed cell walls consisting mainly of the skeleton of lignin-made middle lamellae (**B1**–**B3**).

SRB are a group of prokaryotes that include members of the *Bacteria* and *Archaea* domains. SRB reduce sulphate to sulphur when metabolising simple organic molecules, although any sulphur compound with an oxidation state above −2 can act as an electron acceptor [49] as well as nitrate or nitrite; and even oxygen respiration is possible [46]. The sulphate ion acts as an electron-acceptor in a reaction chain, where the carbohydrate moiety acts as an electron-donor; other potential electron acceptors include Fe(III). A wide variety of organic compounds can act as electron-donors, including phenolic compounds, such as lignin and tannins, although the metabolic process does not involve the destruction of the aromatic ring. However, SRB do not metabolise polysaccharide and phenolic substrates directly, but rather use the by-products of other bacteria as their food source [46]. Thus, the activity of erosion bacteria and soft-rot fungi can stimulate the accumulation of both sulphur and iron. Although the activity of SRBs is dominant in anoxic conditions, some strains are facultative and able to operate in anoxic environments and in low oxygen concentrations [50]. SRB have been found in marine sediments, mud volcanoes, hydrothermal vents, hydrocarbon seeps and hypersaline microbial mats, in extreme pH environments (pH 2–10) [46].

Although thought to be associated exclusively with anaerobic conditions, it has been suggested that aerobic or fluctuating oxygen levels promote the deposition of sulphur in marine artefacts, indicating the importance of the local environmental conditions and their temporal and spatial variation affecting sulphur profiles in the wood even at the same site [51,52]. This includes the potential for localised anaerobic conditions to be produced in the vicinity of oxygen-consuming microorganisms. Modelling of sulphur deposition in wood was studied by immersing fresh pine sapwood samples in a solution of Fe(II) sulphate which was inoculated with a bacterial consortium obtained from seawater. The deposition of thiols in the wood was demonstrated through the use of scanning X-ray spectro-microscopy and sulphur K-edge X-ray near edge structure (XANES) spectroscopy. It was found that the thiols accumulated in the lignin-rich middle lamella of areas of wood that exhibited erosion bacteria attack. The presence of iron sulphides was also demonstrated. It was found that penetration by sulphate-reducing bacteria was restricted to regions of the wood where tunnelling bacteria were active. The generation of hydrogen sulphide by SRB produces a strongly reducing environment capable of changing the oxidation state of metals (e.g., $Fe^{3+} \rightarrow Fe^{2+}$, $Mn^{4+} \rightarrow Mn^{2+}$) [8]. In this way, soluble iron can migrate through the wood to regions of SRB activity and react to form insoluble iron sulphide deposits. The timbers of the Batavia contained a range of iron sulphate compounds and the Mary Rose contained a mixture of reduced sulphur compounds of iron as well as iron sulphate [53]. It has been observed that shipwrecks from the Baltic sea, such as the Vasa, the Crown and the Riksnyckeln tend to show high accumulations of iron and sulphur in the surface regions of the wood, whereas the Mary Rose and the Göta shipwreck from the Swedish west coast show a more uniform distribution of these elements [48]. The Sword shipwreck dating from the 17th Century contains iron-tannin precipitates, which makes extraction using chelates difficult [54]. In the case of the Batavia, a Dutch East Indiaman that sank off the coast of Australia in 1629, the timbers were sealed within a marine concretion that provided an anaerobic environment. Trapped within this concretion were also iron objects, such as cannon and cannon balls, which corroded and reacted with hydrogen sulfide to form pyrite ($FeS_2$) and pyrrhotite (FeS) [55].

In anaerobic freshwater environments, there are usually low concentrations of sulphate ions and the potential for sulphur enrichment of archaeological wood is much reduced, although SRB are still active in oxidising organic compounds, often in combination with methanogens [46]. It is thought that under conditions of low sulphate concentration, that SRB can utilise hydrogen, lactate and ethanol as substrates. The terminal electron acceptor used in the metabolic process depends upon the pH and the redox potential in the local environment [20].

### *2.3. Waterlogged Wood in Saltwater*

Waterlogged wood in marine conditions is usually exposed to two very different environments. In open seawater, the wooden artefacts are susceptible to sediment erosion and degradation by the wood-boring organisms: gribble and shipworm *Teredo navalis*, although the risk of attack of the latter is reduced considerably if the cellulose content of the wood is low. If the wood is buried in the sediments, the limited oxygen availability prevents respiration of wood borers, and only microbial degradation is possible, which often results in a relatively good state of wood preservation [56,57].

Sea salt present in wood excavated from salt waters can crystallise during drying and damage the wood structure. It can also increase water absorption by wood and promote corrosion [58]. However, archaeological wood that has been exposed to hyper-saline environments (e.g., the Dead Sea) shows little sign of physical or chemical degradation, where the presence of salts in the wood act to physically bulk the material, as well as inhibit microbial colonisation [59].

### 2.4. Chemical Degradation

Waterlogged wood exhibits losses of the polysaccharide component primarily. Degradation of the cellulose in waterlogged wood involves a reduction in relative crystallinity, although crystal width appears to be unaffected [15]. Xylan in the oak wood of the Vasa ship was found to be depolymerised with the formation of water-soluble fragments [60,61]. Loss of carboxyl groups associated with glucuronic acid residues in hemicelluloses, as well as some loss of ester linkages in the lignin-carbohydrate complex (LCC) has been reported [15]. Degradation of lignin is much less severe compared to the carbohydrate components, but does involve some loss of β-O-4 linkages and degradation of syringyl moieties [15], as well as minor oxidation, which probably occurs after excavation or before oxygen is consumed following burial or immersion [62–64], but might indicate an oxic phase in the history of the sample [65]. A large increase in fluorescence background in the Raman spectrum was attributed to greater mobility of the lignin structure, due to the breakdown of LCC bonds, as well as a higher relative proportion of lignin in the wood [15]. Lignin extracted from waterlogged wood was characterised by direct exposure mass spectrometry (DE-MS) and compared with lignin extracted from fresh spruce wood [66]. It was concluded that combining this analytical technique with principal component analysis was a promising method for studying lignin degradation in archaeological wood.

Information about the degradation state of the molecular components of waterlogged wood can be obtained using a variety of instrumental techniques, including nuclear magnetic resonance (NMR), pyrolysis mass spectrometry (py-MS), pyrolysis-gas chromatography-mass spectrometry (py-GC-MS), direct exposure mass spectrometry (DE-MS), evolved gas analysis mass spectrometry (EGA-MS) and gel permeation chromatography (GPC) [67–71]. Silylation and py-GC-MS can be used to examine the lignin in waterlogged wood, revealing evidence of natural or anthropogenic heating of the wood [72]. Solid-state NMR of waterlogged wood showed that the hemicelluloses were completely removed, but that the lignin was intact [73]. Signals in the NMR spectrum can be significantly broadened due to the presence of iron ions in the waterlogged wood [74], and solid-state NMR is not sensitive enough to detect some important chemical features. For this reason, there has been an interest in employing ionic liquid dissolution techniques for NMR, sometimes combined with derivatization in order to improve solubility [67]. It is generally observed that the lignin structure is not significantly altered by the ageing process in waterlogged conditions [75]. Fourier transform infrared (FTIR) spectroscopy has been used to characterise waterlogged wood samples in order to determine the extent of bacterial attack, but this method requires prior calibration in order to determine the correlation between the FTIR spectrum and lignin content [76,77]. FT-Raman spectroscopy has also been used for the same purpose [78]. The chemical composition (holocellulose and lignin) of degraded waterlogged wood has been determined by using near-infrared spectroscopy (NIR) in combination with partial least squares regression [79]. The region between 1600 and 1800 $cm^{-1}$ can be used to identify the chemical state of the wood, and the pH can be determined by measuring the band ratios of the peaks at 1710 $cm^{-1}$ (-COOH) and 1608 $cm^{-1}$ (-COO-) [80]. A band at 1400 $cm^{-1}$ in the IR has been assigned to a complex of iron and cellulose oxidation products [81]. Raman spectroscopy has been used to study iron sulphides in waterlogged wood [82]. Electron spin resonance has been used to determine the original charring temperature of charred waterlogged wood [83].

There have been reports of the presence of volatile monoterpenes present in waterlogged archaeological wood, which can be used as an aid to identification [84]. Sesquiterpenes may also be present (abietic, dehydroabietic, neoabietic, pimaric, sandaracopimaric acids), which are derived from the use of pine resins for caulking/waterproofing [75,85]. Oak wood, obtained from the Riksapplet shipwreck dating to 1676 was analysed and found to still contain tannins, particularly ellagic acid, indicating a partial loss of the more water-soluble extractive fraction [75]. Where tannins and iron are present, they can form complexes that are not amenable to extraction [54]. The presence of tannins in oak is an important factor in promoting iron accumulation.

### *2.5. Physical Degradation*

The increase in porosity of the degraded wood due to microbiological degradation results in a higher maximum water content (MWC) and a reduction in residual basic density (RBD) compared to fresh wood from the same species. The MWC (also referred to as moisture content, or maximum moisture content) is the ratio of the dry wood weight to the total weight of wood plus water expressed as a percentage; the RBD is the ratio of the density of the archaeological wood sample compared to a typical value for a fresh wood sample of the same species, also expressed as a percentage. Waterlogged wood is considered to be degraded when the MWC is greater than 150% (depending on species) and severely degraded when the MWC exceeds 400% and RBD is less than 40% [86]. There has been some debate regarding the best method to determine the MWC, with some workers advocating vacuum-pressure treatments of the wood to ensure that all air bubbles are removed, but this carries with it the risk of damage to the wood. A study of pre-treatments concluded that they were unnecessary, but that waterlogged wood must be stored fully in water and immersed in watertight containers prior to any conservation activity and that MWC measurements must be carried out within a few days of sampling [87]. The density of the wood can be used to determine the degree of collapse of the wood when dried from the waterlogged state and hence the most appropriate method of conservation. The weight of the waterlogged wood can usually be readily determined, but measurement of the volume of the wood is not usually straightforward, unless the objects are regular geometric shapes and it is necessary to resort to pycnometric or buoyancy force techniques [88]. Although used as a measure of the extent of wood degradation, there has been found to be no correlation between MWC and holocellulose content, although a clearer relationship between holocellulose/lignin ratio was found, albeit with considerable scatter [89]. Water in waterlogged wood is in different environments depending upon whether it is in the macropores of the wood, or located in the cell wall and density corrections may be necessary to take this into account. It is common to find that wooden artefacts exhibit degradation gradients between surface and interior, upper and lower regions, or between heartwood and sapwood. Average values for samples may not therefore necessarily be that informative when determining the extent of degradation of the whole sample and the appropriate conservation technique to employ.

Porosity determination of waterlogged wood can be challenging to measure. Techniques, such as nitrogen sorption require dry samples and this risks collapse occurring, even when using methods such a solvent exchange or supercritical drying [90]. Porosity measurements on water-saturated samples, such as solute exclusion, thermoporometry, or NMR relaxation may be compromised by the presence of degradation products in the wood. Nitrogen sorption studies of waterlogged wood have shown that there is an increase in mesoporosity [15,91]. Helium pycnometry has been used to determine the cell wall density of degraded waterlogged wood after drying [92].

There has been interest in the use of ultrasound as a means of determining the degradation state of waterlogged archaeological wood in situ [86]. This technique determines the density of the wood by analysing the compression (p-wave) velocity of ultrasound waves propagating through the wood.

The use of dynamic mechanical analysis (DMA) can be used to find the direct relationship between the viscoelasticity of the degraded wood and its chemical composition (precisely, the cellulose content) that translates to the degree of wood degradation. An exponential decrease in the storage modulus ($E'$) and the loss modulus ($E''$) was observed for both waterlogged softwoods and hardwoods. The decrease in $E'$ in heavily degraded wood results from the progressive reduction in the amount of crystalline cellulose fraction in the cell wall, while the decrease in $E''$ is due to the degradation of its amorphous part. The ratio $E''/E'$ ($\tan\delta$) varies with the frequency, depending on the degree of wood degradation; it is higher for slightly decayed wood, while for severely degraded wood, the $\tan\delta$ values at low frequencies are lower (or similar) than for sound wood of the same species. The DMA technique can then serve as a useful tool for identification of the state of waterlogged wood preservation (in both a wet and a dry state), based on the magnitude of the storage and loss modulus and the changes in secondary relaxation peaks in the loss factor (their location and intensity) [42,93].

## 3. Properties of Commonly Encountered Consolidants and Some Case-Studies from the Conservation Practice

Waterlogged wood differs considerably depending on the species, growth anomalies, degree of degradation, permeability or history of use. Therefore, it is impossible to apply one versatile treatment to all wooden objects. To date, different methods and chemicals have been used for wood consolidation and stabilisation, including many treatment types (e.g., bulking, impregnation, in situ polymerisation) and various drying methods (slow air-drying, freeze-drying, polar solvent drying) [94].

The purpose of a consolidant is to prevent the collapse of the treated wood during conservation and drying and to ensure that the wood has sufficient structural integrity that it can withstand handling and display. Early attempts to conserve waterlogged wood used solvents, oils or waxes, but these failed to provide sufficient support to the degraded wooden objects [95]. Historical chemical methods include an alum treatment [96] and more recent treatments with PEG and sugars [97]. From the mid-1800s until the 1950s many waterlogged finds (especially in Scandinavia) were treated with alum ($KAl(SO_4)_2 \cdot 12H_2O$), which was used to treat many artefacts of the Oseberg find, dating from 834 AD, which was excavated in 1904 [67]. Over time, this has resulted in significant conservation problems due to the presence of sulphuric acid which has severely degraded the wood. With great good fortune, the wood of the ship was not SO-treated. The alum treatment involved the soaking of wooden artefacts in concentrated alum solutions at 90 °C for up to 36 h [5]. This resulted in two distinct regions within the larger wooden objects, with a hard alum-rich outer zone and a softer alum-poor inner zone. The treated wood is now highly acidic (pH 1–2.5) and it has been found that the carbohydrate component of the wood is absent and the lignin is highly oxidised. Apart from alum, there are other inorganic components present and it is thought that the presence of iron, in particular, might have a catalytic effect on the degradation process [98], but this is not certain. For example, during reconstruction, an iron rod was used to strengthen the sled and other objects contain remnants of the original iron nails. Although decorative iron nails were removed from most objects prior to treatment, they were later replaced. Other inorganic components include zinc and mercury from the treatment of the wooden objects in zinc containers containing a solution of mercuric chloride, used as a biocide. Many of the alum treated objects were subsequently impregnated with linseed oil either by immersion or by brushing until fully saturated. The reconstructed objects were then coated with a matt varnish to remove the shine caused by the linseed oil treatment. An epoxy-based coating was also applied during the 1950s. The linseed oil-impregnated region provides the only remaining structural integrity for many of the finds and appears to limit the diffusion of sulphate into the treated areas [99]. Although not used on the Oseberg finds, glycerol was often added to the alum-treatment solution after 1910, which means that objects SO-treated are now extremely sensitive to ambient relative humidity. The alum-treated zones of the Oseberg objects show pH values ranging from 1 to 4.5, with the source of acidity being the alum. During the impregnation process, the heating of the alum solution to 90 °C results in a drop in solution pH from 3.5 to 2, due to the precipitation of alunite ($KAl_3(SO_4)_2(OH)_6$), which is only formed in heated solutions. This reaction results in the production of excess sulphate ions, which enter the wood structure [96]. The use of alum was the standard method for the treatment of archaeological wood at the Danish National Museum in Copenhagen, where it was in use for a century [100]. The Hjortspring boat was treated with a mixture of alum and glycerol in the 1920s, but the hygroscopic properties of this mixture caused stability problems and the boat was re-treated between 1966 and 1979 with PEG solution. Alum was also used to treat the County Hall Roman ship that was found in London in 1910, but very little of this artefact now remains.

Currently, polyethylene glycol (PEG) is the most common conservation agent. PEGs are linear polyethers with terminal hydroxyl groups, commercially available in a wide range of molecular weights from 300–600 (liquids at room temperature), through 1000–1500 (semi-liquids), to 3250–6000 (wax-like substances), freely soluble in water or alcohols and easy to use [101–105]. PEGs are hygroscopic, and exhibit deliquescence associated with a large increase in sorbed water at a critical air relative humidity (RH) [106], which depends upon temperature, molecular weight (MW) of polymer and the presence of any additives. This can cause problems for artefacts that are not located in controlled humidity conditions. The oxygen atoms of the PEG backbone and the terminal OH groups of the polymer chain can both form hydrogen bonds with the sorbed water molecules. As the polymer chain length increases there is a reduction in the proportion of terminal OH groups and in the entropy of mixing of the polymer with water molecules. This results in a decreased solubility of higher MW PEGs in water, which plateaus at an MW of approximately 6000, with little change in solubility thereafter. Increasing the temperature will increase the solubility of the PEG in water, requiring heating when treating with longer chain PEGs which can cause technical problems when treating large objects. The penetration of PEGs into wooden objects depends upon the MW and the degradation state of the artefact. There is no single PEG that can stabilise both lightly and heavily degraded waterlogged wood. High MW PEGs are suitable for stabilising heavily degraded waterlogged wood, but are unable to penetrate the microporous structure of the wood, whereas low MW PEGs can penetrate wood easily but are not solid at room temperature as well as being hygroscopic. By using a two-step treatment, the low MW PEG is able to stabilise the heavily degraded wood and this is then protected by an envelope of high MW PEG so that hygroscopicity is not a problem.

PEG was first used in the preservation of wooden artefacts after research at the Forest Products Laboratory in Madison WI in the 1950s [107–110]. The diffusion of PEG into waterlogged wood is a slow process, which is influenced by the MW and composition of the consolidant, the orientation of the wood sample with respect to the diffusant, anatomical characteristics of the wood and extent of deterioration of the wood, as well as physical conditions, such as the temperature of treatment [111]. Heavily degraded wood with a low density will exhibit severe collapse on drying and is usually treated with high MW PEG, followed by freeze-drying. Waterlogged wood that is less degraded can be treated with low MW PEG prior to freeze-drying [88]. Conservation usually involves a two-step treatment using a low and then a high MW PEG. Two-step treatments have been employed for many conservation projects including the Mary Rose in the UK, the Kinneret boat in Israel, the Bremen Cog in Germany, the Vasa in Sweden, the Shinan Treasure Ship in Korea, the Copper ship in Poland and the Hasholme logboat in Hull, UK.

The Mary Rose sank off Portsmouth (UK) in 1545 and the site remained largely undisturbed until 1965. It was decided to raise and conserve the ship in 1978. She was raised in 1982 and the mainly oak timbers were initially sprayed with fresh, chilled water for 12 years to remove the marine salts. From 1994 until 2013 she was conserved using a two-step PEG treatment which involved continuous spraying with an aqueous solution of PEG 200 (40% $w/w$) for 12 years followed by spraying with a heated aqueous solution of PEG 2000 (60% $w/w$) for a further 7 years. During the spraying operation, a broad spectrum biocide was added in order to prevent microbiological degradation during the conservation process. This was followed by a controlled air-drying process at 55% RH and 20 °C. During this time, additional PEG 4000 was brush-applied to selected parts of the timbers [112–114].

The Kinneret boat (called by the press "Boat of Jesus"), dated back between the 1st century BC and 2nd century AD, was excavated from the muds of the Sea of Galilee in 1986. A two-step PEG treatment was chosen to conserve at least seven various types of wood in different states of degradation. The conservation process started with using PEG 600 with an increasing concentration up to 50%, then PEG 3500 was applied, and the concentration was slowly increasing up to 90%. The immersion method was proposed to shorten the conservation time to seven or eight years. Thirty-five tons of PEG were used during the process [115].

The conservation of the Bremen Cog of 1380 took 38 years from excavation to displaying the artefacts to the public. The ship was reconstructed in the display hall by suspending the wooden pieces from the ceiling and building a conservation tank around the hull [30,116]. The consolidation process involved treatment using two consecutive baths of aqueous solutions of PEG 200 and PEG 3000. The Bremen Cog was treated in the low MW PEG bath for ten years. It was found that the low MW PEG solution very quickly became contaminated with bacteria, resulting in the solution becoming very cloudy, which was dealt with by adding a flocculant and passing the solution through gravel filters. At the end of the impregnation procedure, it was necessary to dispose of 1600 tonnes of used PEG solution. It was established that PEG 200 was completely biodegradable in municipal wastewater treatment facilities, which allowed for the disposal of the drains at a slow rate. The treatment with PEG solution was simplified because PEG 200 is a liquid at room temperature and could be pumped directly into the conservation tank. However, PEG 3000 is solid at room temperature, requiring the PEG to be delivered using lorries with heated tanks so that the hot PEG could be pumped together with water into the treatment tank. Treatment with PEG 3000 was initially at a concentration of 60% in water, which was later increased to 70%, requiring a temperature of 40 °C to keep the PEG in solution. Treatment with PEG 3000 took three years. Once the conservation tank had been removed it was necessary to remove the surface encrustation of PEG 3000 to expose the treated wood surface. Residual shrinkage of the treated wood ranged from 0–2.7%, compared to 14.5% for untreated timbers.

The Vasa sank in Stockholm harbour in 1628 and was re-discovered in 1956. She was recovered from Stockholm harbour in 1961 and the timbers were treated with aqueous solutions of PEG 600, 1500 and 4000, with some additional manual applications of PEG 4000 and 1500 to selected parts between 1962 and 1965. The wood was sprayed using an aqueous PEG 1500 solution from 1965 to 1971, followed by PEG 600 from 1971 to 1979. PEG 600 and 4000 were applied manually between 1979 and 1991 with the excess PEG 4000 melted off the surface [117]. The presence of PEG 600 makes the Vasa sensitive to changes in RH, since PEG 600 is hygroscopic [117]. The timbers of the Danish Skuldelev ships which were found in Roskilde Fjord in the 1960s were treated in a single-stage process by submersion in a tank containing an aqueous solution of PEG 4000 followed by freeze-drying.

The excavation of the Shinan treasure ship, a medieval Chinese vessel found in the waters of the south-western coast of the Korean peninsula, took nine years, from 1976 to 1984. Her priceless cargo was excavated along with the ship that included 28 tons of copper coins, sandalwood, sherds, and plenty of metal, stone, and other objects. A two-step PEG treatment was applied to the ship's Chinese red pine and Chinese fir timbers. It started with the removal of iron corrosion products. Then wooden elements were immersed in a 5% solution of PEG 400 at room temperature. The concentration was raised by 5% up to 20% in 3–4 month intervals. Then the impregnation continued in 25% PEG 4000 solution at

40°C, and the concentration was raised every 2–3 months by 5% up to 75%. Small heavily degraded parts were treated only with PEG 4000 [118].

The Copper ship, found in the Gulf of Gdańsk, Poland, was built in 1400 and served only eight years. She sank due to a fire during her route from Gdańsk to Western Europe transporting metal and woodland products. Surprisingly, the excavated wooden parts (mainly oak) remained in a well-preserved state despite 567 years of submersion in the sea sediments and salt water. The first conservation employed slow drying and surface impregnation with linseed oil and turpentine. Then, in the 1980s, when PEG was introduced as a new consolidant, it was employed for Copper ship conservation as well. The treatment involved the application of increasing concentrations (from 10% to 70% or 90%) of a mixture of lower MW PEGs (400 and 1500) or PEG 4000 using different methods, including soaking in warm PEG solutions (higher temperature increases the rate of PEG diffusion into the wood), spraying or paint brushing, adding biocides to prevent microbial activity in the conservation solution. Impregnation lasted from one up to three years, followed by slow air-drying of the artefacts until they reached moisture equilibrium with the surrounding air. Two-step impregnation was applied on an 8 metres long starboard, starting with spraying with an increasing concentration of PEG 300 (from 10% to 40%), followed by applying 40–50% solution of PEG 3000. No cracks were observed in the treated wood, the ASE was 73%, but wood hygroscopicity increased significantly due to a mixture of PEG 300 and 3000 present on the wood surface [119].

The Iron Age oak dug-out Hasholme logboat was discovered in 1984 at the Hasholme site in the parish of Holme-on-Spalding Moor in East Yorkshire, UK. After excavation, it was stored at the National Maritime Museum for two years and then transported to Hull, where it was conserved by spraying with PEG for 19 years (a two-step treatment). At the end of 2009, the conservation was completed, and the boat was left for natural air-drying after being washed down to remove the remains of PEG and the mould from its surface. A biocide was applied to prevent further mould growth. Some parts (e.g., the large decorated transom) were freeze-dried. Today, the boat is displayed in the Hull and East Riding Museum galleries under controlled humidity conditions to prevent further wood shrinkage or cracking and is regularly monitored for any signs of deterioration [120,121].

The Yenikapı Byzantine-Era Shipwrecks, Istanbul, Turkey were placed in desalination tanks after excavation where salt was removed in a running water bath, iron traces were then removed using disodium EDTA and oxalic acid followed by treatment in flowing water, with a repetition of the process until the iron was removed entirely. For conservation, both PEG and Kauramin (melamine formaldehyde) were employed, with the Kauramin treatment reserved for highly degraded non-durable materials. The other objects were soaked in a solution of 45% PEG 2000, followed by freeze-drying [122].

In order to determine if the consolidation process is complete, it is important to know the concentration of PEG inside the wood. Methods to determine PEG in solution include gravimetric and refractometry, but determination in wood requires extraction combined with an analysis technique, such as thin-layer chromatography (TLC) or high-performance liquid chromatography (HPLC). Semi-quantitative information can be obtained using TLC, but much more accurate information is obtained using HPLC, or size exclusion chromatography (SEC). However, such procedures can be time-consuming. It is known that PEG forms coloured complexes with bismuth, cobalt, molybdenum or iodine compounds and the reaction of aqueous solutions of PEG of different molecular weights (MW) with Dragendorff reagent (a mixture of bismuth subnitrate, hydrochloric acid and potassium iodide) has been examined. No reaction was observed with PEGs of MW 200–600, but a concentration-dependent change in the spectrum was observed with PEGs with an MW of 2000 and above. The colourimetric method was found to be MW-specific and the spectrum of admixtures of PEG 4000 was unaffected by additions of PEG 300. The method was applicable to PEG extracts from treated wood samples. Low MW PEGs for 200–400 did not interfere with the analysis [123]. In-situ Raman spectroscopy has been used to quantify the level of PEG in waterlogged archaeological wood, in order to avoid the need for removal of samples and using extraction techniques [124]. Magnetic resonance imaging has also been used to visualise the distribution of PEG in waterlogged wood [125].

Impregnation with PEG in hot baths over extended periods can result in the relaxation of growth stresses, resulting in the distortion of treated timbers. It is also known that PEGs are susceptible to thermal-oxidative degradation under accelerated conditions, resulting in the formation of lower MW fragments which may be a concern for the long-term stability of conserved objects [53,117]. Examination of the distribution of PEG in treated wood from the Vasa and the Danish Skuldelev Viking ships showed that although large amounts of PEG could be extracted from degraded wood, there was very little found in the sound parts [117]. PEG 4000 was found only in the surface layers of the wood, whereas PEGs 1500 and 600 were found at all depths. Low MW PEG was detected in one of the Skuldelev ships which was thought to be due to degradation of the PEG 4000, but there was no evidence of degradation otherwise. However, if the starting material composition is not known, it is difficult to eliminate degradation with certainty. An alternative approach is to measure formic acid, which is a degradation by-product of PEG; although there may be other sources [53].

Alternatively to polyethylene glycols, sugars (mainly lactitol, less frequently trehalose or a mixture thereof) have been commonly applied for waterlogged wood conservation since the late 1980s. Conservation treatment includes impregnation with heated or unheated sugar solutions; it is appropriate for both large and small objects and can be applied as a pre-treatment followed by freeze-drying. The method provides several benefits to the treated wood, including increased strength, good dimensional stabilisation, and natural colour, being entirely reversible, safe, and more cost-effective than PEG treatment. However, sugars are highly susceptible to microbial attack, and biocides must be added to the impregnation solution [97,126].

Nowadays, more than thirty museums and private conservation laboratories worldwide use lactitol for waterlogged wood conservation. Among the largest artefacts treated with this method are the Poole logboat and the Friesland Smalschip. The pure "cold" lactitol method was applied, inter alia, for the conservation of 4 m-long elements of a pipeline from the Nango oohigashi site in Nara Prefecture, Japan (dated back to the 5th century AD), and included pre-treatment, decolouring and washing (1 month), impregnation with lactitol (3 years), drying at 50 °C (1.5 months), surface cleaning and further drying (0.5 months). A six metres long waterlogged pine coffin, dated back to the end of the 3rd century AD, excavated in 1995 from Simoikeyama tomb in Tenri City, Japan, was conserved using the "warm" lactitol method. The treatment included pre-treatment, decolouring (water plus 1% EDTA-2Na) and washing (1 month), lactitol impregnation at 50 °C started from a concentration of 40% up to 60% (13 months), dusting with pulverised monohydrate lactitol crystals to initiate crystallisation, drying at 50 °C (2 months), surface cleaning and further heat-drying. The total time of the treatment was 16 months. The "warm" lactitol plus 10% trehalose mixture method was applied to conserve the 1st-century BC heavily degraded waterlogged wooden figures excavated at the tomb of one of the kings of the ancient Shisui Kingdom (Han dynasty, 1st c. BC) in Shanzhuang village, China. The treatment included the removal of iron ions (water plus 1% EDTA-2Na, 1–2 weeks), washing in water (3 weeks), impregnation with a mixture of lactitol, 10% trehalose in water and 0.01% Kathon CG biocide at 50 °C started from 15% solution up to 50%, then the temperature was raised to 60 °C, and the impregnation was continued using 65%, 70% and 80%, subsequently (3 months for few centimetres thick artefacts, 6 months for thicker objects up to 10 cm, 18 months for the thickest ones), dusting with pulverised lactitol monohydrate crystals to initiate crystallisation, air-drying, and surface cleaning. The results of the applied treatments were assessed as satisfactory [97].

Consolidants historically used in waterlogged wood conservation are listed and briefly described in Table 1.

**Table 1.** A historical overview of waterlogged wood consolidants [127].

| Consolidant | Exemplary Conservation Methods | Comments |
|---|---|---|
| | Inorganic compounds | |
| Aluminum sulfate | Parts of the Oseberg find were boiled in aluminium sulfate in 1913 by Gustafson, dried and then impregnated with linseed oil. | Good dimensional stabilisation, wood sensitive to moisture changes, deposits on wood surface; no longer in use. |
| Aluminum potassium sulfate (alum) | The method first described by C.F. Herbst (and Speerschneider) in 1861—boiling an object in supersaturated alum solution, then drying and dipping it in linseed oil. The method used in the Danish National Museum (1858–1958) for more than 80% of all waterlogged wooden artefacts collected; applied to some parts of Oseberg Ship in Norway. | Prevents shrinkage, crystals can destroy fragile cells, wood is brittle, prone to cracking and deformations, deposits on the surface, iron elements must be removed, no longer in use. |
| Boron compounds | The Thessaloniki process for medium-degraded waterlogged wood described by Borgin (1978)—soaking wood in a concentrated solution of sodium tetraborate with sodium silicate and an organic polymer. After drying, wood is treated with a concentrated barium hydroxide solution to force precipitation of barium borate and barium silicate inside wood tissue. | Wood stabilisation and appearance are not always satisfactory; no longer in use. |
| Chromium compounds | Conservation by exchanging water in wood for a 2–10% solution of chromium(VI)oxide with the addition of 10–20% sodium dichromate (1965, French patent by Garrouste). Bouis proposed a similar method in 1975 but with the addition of linseed oil after drying (chromium compounds harden linseed oil). | Good dimensional stability, low weight and high porosity, resistance against fungi and fire, brittle, unnatural colour, the high toxicity of the chemicals; hardly used. |
| Silicon compounds (sodium and potassium silicate) | Scoot (1921–1926) applied silicon glass for restoration objects in the museum; Cebertowicz and Jasienski (1951) used a mixture containing water glass by electrokinetic method on wooden elements in Biskupin, Poland; a dugout canoe consolidated by slow drying and brushing with a sodium silicate solution (Plenderleith). | Improved strength and hardness, cracks can close, unaesthetic appearance, irreversible; alkali silicates or water glass are no longer in use. |
| | Organic compounds | |
| Animal glues | Glue solutions used for conservation of dugout canoes in Switzerland (1850–1900); Rathgen (1924) proposed using an aqueous glue solution in combination with drying and impregnation with resins; waterlogged wood conservation in Hungary (1959). | Glues are sensitive to moisture and microbial attack, shrink and become brittle, have poor penetrability, darkened wood colour; no longer in use. |
| Linseed oil | Oseberg Ship treated with creosote and linseed oil (since 1904) or linseed oil and white spirit (1957), parts of Oseberg Ship and funeral artefacts treated with linseed oil (1913); a boat treated with a mixture of turpentine, linseed oil, colophony and Carbolineum (1958). | Insufficient stabilisation, no longer in use. |
| Tung oil | Used for surface treatment of parts of the Hjortespring Find (Denmark) impregnated with alum (1921). | Poor strengthening effect, spotting on the surface, unnatural brown colour; no longer in use. |
| Lanolin | Lanolin method proposed by Vynckier (1982/83). | Method not important in wood conservation. |

**Table 1.** *Cont.*

| Consolidant | Exemplary Conservation Methods | Comments |
|---|---|---|
| Beeswax | Small wooden artefacts heated in a mixture of rapeseed oil, wax, spruce resin and benzene by Speerschneider (1861); pouring melted wax on a wooden object (1924); protective coating of melted beeswax for wood treated with alcohol and resin (1979). | Sometimes used for small and fragile artefacts, or as a compound of some conservation mixtures. |
| Carnauba wax | Dehydrated waterlogged wood submerged in melted paraffin, then in a mixture of dammar, carnauba wax, paraffin and beeswax by Brorson Christensen (1949–1956). | High durability, good stabilisation effect; no longer in use. |
| Paraffin | Dripping or pouring melted paraffin on wood, or storage in liquid paraffin (1924); wood dehydration with methanol and toluene, then impregnation with melted paraffin (Leechman 1929); dehydration with ethanol prior to paraffin treatment (Kisser and Pittioni, 1935); the paraffin method used in Hungary (1950–1960). | Good dimensional stabilisation for soft objects with low density; occasionally used for small highly degraded artefacts and wood/metal composites. |
| Microcrystalline wax | Mentioned as waterlogged wood consolidant by Werner (1959) and Sujanova (1972). | Not used for wood stabilisation. |
| Dammar | As a component of a conservation mixture (1949–1956); the alcohol–ether–dammar method described by Plenderleith (1956); wooden writing tablets treated with dammar after water–methanol–ether exchange (Blackshaw, 1974). | Good consolidation effects for heavily degraded wood, appropriate for smaller objects; chemicals applied pose a risk of explosion and fire; not commonly used. |
| Colophony | The acetone–rosin method published by McKerrell (1972); used for conservation of hardwood objects such as dead eyes, pulley blocks, and other ship's fittings by Fox and for inlays of wood and ivory of a sword handle by Payton (1987). | Good dimensional stabilisation, suitable for low-permeability hardwoods; occasionally applied for better-reserved small objects. |
| Shellac | Alum-treated wood coated with shellac after drying and brushed with linseed oil (Herbst 1858–1860); heavy waterlogged object dewatered with glycerol and dried can be coated with a shellac solution (Plenderleith, 1956). | Low weight of treated object, good dimensional stabilisation; not in use anymore. |
| Ethylene glycol | Soaking wood with ethylene glycol until the final treatment (Miihlethaler, 1969); used to swell dried and shrunken waterlogged wood (De Jong, 1977); as an anti-shrink agent in the Thessaloniki process (Borgin, 1978). | Insufficient wood swelling by low-molecular glycols; rarely used. |
| Glycerol | For storing and soaking of wooden artefacts (1900); mixed alum–glycerol treatment (Brorson Christensen, 1910); Celtic monumental sculpture treated with rosin/glycerol (after 1911); parts of the Hjortespring Boat treated with glycerol (method developed by Rosenberg, 1921); as pre-treatment followed by freeze-drying (1986). | Crack formation or warping can occur, very hygroscopic; not in use. |

**Table 1.** *Cont.*

| Consolidant | Exemplary Conservation Methods | Comments |
|---|---|---|
| Polyethylene glycols (PEGs) | Recognised as suitable consolidant for waterlogged wood by Moren and Centerwall (1961) and Stamm (1956); parts of Oseberg Ship treated with melted PEG 4000 by Rosenqvist; the beginning of the conservation of the Vasa ship in Sweden (1961); conservation of the Bremen Cog (recommendations by Noack, 1965); treatment of parts of the Sjøvollen Ship in Norway (1968); PEG pre-treatment followed by freeze-drying developed by Iwasaki and Higuchi and Ambrose (1969–1970); the beginning of the Mary Rose conservation, Great Britain (1982). | Direct exchange of water by PEG, good stabilisation effect, darkened wood colour, high weight of the treated object, susceptible to microbial degradation, corrosive to metals, not stable in the long-term; the most common conservation method for waterlogged wood. |
| Sucrose | Noack proposed sucrose for the Bremen Cog treatment (1965); Franguelli and Loda (1970–1972) investigate wood conservation with sucrose; sucrose as a pre-treatment to freeze-drying (Parrent, 1983); | Good stabilisation and consolidation effect, best for better-preserved wood, natural wood appearance; used for objects of not particular historical value, when PEG-treatment is too expensive and time-consuming. |
| Sugar alcohols | Suitability of mannitol and sorbitol studied by Barbour and Murray (1982); mannitol as a pre-treatment followed by freeze-drying (Murray, 1985); two-stage treatment with mannitol and PEG prior to freeze-drying (Imazu, 1988); treatment of a 6-m-long wooden coffin (1998) and dugout pipeline (1999). | Insufficient stabilisation and white deposits—mannitol, better results for lactitol; not commonly used. |
| Cellulose ethers | A wooden coffin treated with Methyl cellulose solution (Schlabow, 1961); reports about not satisfactory results of methyl cellulose impregnation (Van der Heide, 1963; Ankner, 1969). | Reversible, but not suitable as consolidants because of poor penetration; not in use. |
| Cellulose esters | Nitrocellulose varnish used for sealing of the alum-treated parts of the Hjortespring Find, Denmark (1921); treatment of wooden scabbard with a solution of celluloid in amyl acetate and acetone (Plenderleith, 1954). | Low penetration, insufficient strengthening, brittleness of treated objects, nitrocellulose is highly flammable; not in use. |
| Phenol-formaldehyde resins (PF resins) | Considered as waterlogged wood consolidant since 1965–69 by Noack and Mühlethaler; USSR patent by Vichrov (the method of Minsk) for conservation of archaeological artefacts (1972); combined treatment with sucrose solution and phenol alcohol by Kolčin (1973), and sucrose with PF resin by Kazanska and Nikitina (1984). | Not suitable for large objects due to the short hardening time, imparts dark colour; not in use. |
| Urea-formaldehyde resins (UF resins) | First experiments with water-soluble UF resins (Celodal, 1938) and with hardening using a catalyst (von Stockar 1938); conservation of wooden bucket (1968); a combination of UF resins with alum (Szalay, 1980). | Not suitable for large objects; rarely used. |
| Melamine-formaldehyde resins (MF resins) | Used for waterlogged wood conservation since 1957 by Mueller-Beck and Haas; successful conservation of a paddle with Piazep ME/2 by Cott (1968); application of Kauramin CE 5549 for conservation of coat and ship elements by Witköpper and Hoffmann (1998). | Sufficient penetration and stabilisation, wood can bleach; occasionally used for smaller objects. |

**Table 1.** *Cont.*

| Consolidant | Exemplary Conservation Methods | Comments |
|---|---|---|
| Polyvinyl compounds | Poly(vinyl acetate) used for preliminary conservation of waterlogged wood (Losos, 1958); further experiments on the method by Brorson Christensen (1970). Poly(vinyl alcohol) used by Losos (1958); a mixture of Poly(vinyl alcohol) and glycerol for wood conservation used by Rumâncev (1958); medieval artefacts consolidated by Müller and Thieme (1966). Gilroy used Poly(vinyl butyral) to conserve a pulley shave from the Dutch ship Zeevijk in 1978. Poly(vinyl chloride) was tried for spoon conservation by Ypey in 1964. | Poly(vinyl acetate) is not hard enough for wood stabilisation, low dimensional stabilisation; Poly(vinyl alcohol) is reversible, poor dimensional stabilisation; Poly(vinyl butyral) has poor penetrability, gives good strengthening effects; not in use. |
| Poly(methyl methacrylate) (PMMA/MMA) | Used for in situ polymerisation in waterlogged wood by Brendel in 1966 and Munnikendam in 1967. PMMA used for the conservation of some artefacts from the Oseberg find stored in formalin by Rosenkvist. | MMA requires wood dehydration which can lead to its shrinkage, heat released during polymerisation can cause warping or shrinkage in wood; PMMA has a plasticising effect, wood can swell; occasionally used for small artefacts. |
| Poly(ethyl methacrylate) | Sawada used a solution of Paraloid B72 in xylene for consolidation of a vermilion Japanese lacquer vessel (1981). | Used only in exceptional cases. |
| Poly(butyl methacrylate) (PBMA/BMA) | Bowls, spoons, arrows, spheres, and wedges of wood treated with BMA by Nogid and Podzdnâk (1964/65); modification of the method by De Jong (1977). | Strength improvement, colour and grain pattern not changed; rarely used. |
| Poly(2-hydroxyethyl methacrylate) (HEMA) | In situ polymerisation of HEMA in oak samples by Munnikedam (1967) resulted in crack formation; modification of the method by De Jong (1975–77) using different catalysts; the method considered by Grattan as less effective than others (1982). | Good strength improvement; can lead to crack formation; not used in practice. |
| Styrene | Neolithic ash samples treated with styrene by De Guichen et al. (1966) without satisfactory results; impregnation of wood after an exchange of water with a mixture of styrene and acrylonitrile using irradiation polymerisation (1970). | Improvement in wood strength, suitable for artefacts destroyed by insects or fungi, wood becomes brittle and hard; sometimes used for small wooden objects. |
| Unsaturated polyester resins | Application of resin to wood filled with acetone after water exchange by Ketelsen (1959) resulted in 7% wood shrinkage; using irradiation curing for styrene/polyester treated wood (De Tassigny and Ginier-Gillet, 1979); consolidation of a freeze-dried wood with Ludopal U 150 and irradiation curing (Schaudy et al., 1985); poly(caprolactone) oligomers tested for the conservation of waterlogged wood by Gerasimova et al. (1981) | Permanent and homogenous strengthening, cracks close upon curing, resistant to UV radiation and moisture changes; used occasionally for small artefacts. |
| Epoxy resins | Used only for dewatered (dried) wood; alum-treated parts of Oseberg Ship were sealed with Epolack (1954–56); conservation by brushing the surface of dugout canoe (Werner, 1961); treatment of a woven helmet by Bill (1979). | Resistant to biodegradation, does not improve wood dimensional stability, can deepen wood colour and produce a gloss on the surface; rarely used for already dried wood. |
| Polyurethanes | Used for glueing PEG-treated wood by Noack (1965). | Not used for consolidation, it can serve as a protective foam. |

**Table 1.** *Cont.*

| Consolidant | Exemplary Conservation Methods | Comments |
|---|---|---|
| Organosilicon compounds | The hull of Vasa ship sprayed with a mixture of PEG, borax, boric acid and methyl polysiloxane (1965); tetraethoxysilane (TEOS) tested for waterlogged wood by Semczak (1975); acrylate dimethylsiloxane oligomers tested by Yashvili (1975); a canoe treated with TEOS by Bright (1979); in situ polymerisation of organosilicon compounds mentioned by Xu (1983). | Good dimensional stability, hydrophobizing effect, TEOS reverses wood grain pattern, white deposits on the surface, wood becomes brittle; acrylate-siloxane oligomers preserve natural wood appearance; rarely used. |

## 4. Properties of Consolidated Wood

### *4.1. Drying of Consolidated Wood*

Once a wooden artefact has been treated with a consolidant and is stabilised, it is then necessary to dry the object so that it can be displayed. Depending on the size of the artefact and the budget available, the main choices are air drying, freeze-drying or supercritical drying. With most large objects, air drying is the only viable option. During the drying process, the wood may be subject to shrinkage or collapse, due to water being removed from the pore structure of the wood and surface tension forces operating at the meniscus surface of the water in the pores. Even sound wood exhibits shrinkage and even collapse when dried, but archaeological wood is especially prone to collapse because it is seriously weakened due to degradation. Consolidants mitigate this collapse occurring because they fill the pore spaces of the degraded wood, but damage can still occur if the drying is not performed properly. It is also essential that the consolidant enters the pore spaces of the degraded cell wall as well as the larger voids in the wood. If air drying is the chosen method, then it is important to carefully control the temperature and humidity of the environment to ensure that the drying does not take place too rapidly, requiring long drying times for large objects [128]. The surface tension collapsing forces at the water/wood interface can be reduced by incorporating other solvents, or by using solvent exchange to ensure that the final solvent is of low polarity, but this can add to the costs and introduce safety concerns. Where the wood has already collapsed prior to consolidation treatment, the options for recovering the original dimensions are limited, but there has been use of treatment with a low concentration of aqueous NaOH solution, or with a urea/ethylene diamine/PEG 200 mixture to swell the wood [129].

Consolidation with PEG prior to drying gives the best results when a low MW PEG is used to prevent cell wall collapse and a higher MW PEG is used to give the wood some structural strength [101]. Drying conditions can affect the distribution of the lower MW PEG in the cell wall, since a concentration gradient is set up between the PEG solution in the lumens and the cell wall, which encourages further diffusion of the PEG under slow-drying conditions, which can be advantageous [130].

Freeze drying is a relatively expensive process that requires long process times, expensive equipment and is not normally used for large conserved objects. The process involves the formation of ice in the object, which is then removed by sublimation under a vacuum. Since ice is of lower density than water, the freezing process involves an expansion that could damage artefacts and for this reason, a cryoprotectant is required. Most commonly, a low MW PEG is used as the cryoprotectant, but mannitol, trehalose, lactose, sucrose and many others are suitable. A successful freeze-drying process is one that occurs without collapse, shrinkage or cracking of the artefact under treatment. When performed correctly, freeze-drying of wooden artefacts after consolidation has been shown to result in reduced shrinkage after drying [131,132]. In order to prevent the collapse of the treated wooden artefact, it is necessary to keep the temperature inside the object lower than the eutectic PEG-water solution, so that there are no liquid phases present and only sublimation of the ice occurs [104,133]. The presence of liquid phases during the sublimation of the ice would give rise to the capillary forces which cause the collapse of the wood structure [12]. Problems arise because these necessary conditions can result in very long drying times for large objects, with low temperatures required in order to maintain a solid PEG/water phase, but higher temperatures being favourable to more rapid drying and careful optimisation is required to minimise costs. Large objects also require custom-made dedicated equipment, which adds considerably to the expense of conservation. Supercritical drying has been examined as an alternative to freeze-drying, but is also expensive, only suitable for relatively small objects and requires an intermediate solvent-exchange step [134]. In other cases, larger objects have been sawn into sizes suitable for the available equipment, as was carried out for the Carpow logboat [135].

### 4.2. Sorption Behaviour

Sorption isotherms of PEG-treated wood show much higher moisture uptakes at relative humidities in excess of 50% [136]. Wood treated with a variety of different PEG solutions showed lower EMC below 80% RH, but much higher levels of sorption thereafter [137]. Archaeological oak wood treated with PEG exhibits a reduced moisture uptake at RH below 80%, but greater moisture uptake above this value [138]. Similar behaviour is observed with pure PEG or PEG combined with pharmaceutical formulations [106,139]. It is often assumed that PEG in the cell wall exhibits lower hygroscopicity due to immobilisation caused by the surrounding cell wall polymers and that changes in hygroscopic behaviour are solely attributable to PEG in the lumens and large void structures [140]. If PEG is essentially immobilised in the cell wall and not responsible for sorption changes, then it should be possible to determine the location of the PEG by examining the sorption behaviour at different PEG loadings. There is also a large reduction in sorption hysteresis observed with PEG-treated wood, whereas untreated ancient oak shows increased sorption hysteresis [141]. Wood treated with a mixture of lactitol and trehalose also showed a reduction in sorption compared to untreated wood, except at RH levels in excess of 90%, as well as a marked reduction in hysteresis [142]. Two explanations can be given for the reduced moisture uptake at lower RH:

If the EMC is determined on the basis of the mass of the sample (e.g., wood plus consolidant) then even at the same level of moisture uptake as untreated wood a lower EMC will be recorded. In order to determine whether the reduction in EMC is genuine, it is necessary to determine the EMC on the basis of wood mass only (sometimes referred to as the reduced EMC).

If the PEG has entered the cell wall, there is a bulking effect and some of the cell wall volume is no longer available to accommodate sorbed water molecules. This property will depend on the extent of the penetration of the cell wall.

The reduction in hysteresis can be attributed to a plasticisation effect on the substrate caused by the consolidants in combination with the sorbed water. This will have the property of reducing the glass transition temperature of the wood cell wall matrix, resulting in a decrease in sorption hysteresis [143,144]; assuming that water molecules are able to penetrate the PEG-cell wall polymer void system. Higher MW PEGs do not enter the sound cell wall [145], but the extent of penetration of the pore structure of degraded wood by PEGs of different sizes is not known. Nanopores exhibit a partitioning effect on solutions of PEGs of different MW (and radius of gyration) and that changing the concentration of PEG in solution influences the radius of gyration [146]. Even if the cell wall pore structure of the cell wall of degraded wood was completely filled by PEG (which seems unlikely) the molecular dynamics of PEG in the wood would still allow for the transport of water molecules through the PEG network, including PEG in the cell wall voids. Furthermore, the changes in creep behaviour of wood afforded by impregnation with PEG (next section) suggest an intimate association between the PEG molecules and those of the degraded cell wall, a property that is also affected by the presence of sorbed water. The molecular dynamics of the interaction of PEG with cell wall polymers has been analysed using high resolution solid-state 13-C NMR, showing that there is, indeed, an interaction between PEG and the cell wall polymers [147,148].

Wood samples treated with alum are not as sensitive to relative humidity as freeze-dried archaeological wood, since potassium alum and ammonium alum salts are not hygroscopic in the range 30–75% RH at 20 °C [95]. However, changes in RH levels can lead to stresses occurring between alum-rich and alum-poor zones in the treated wood, resulting in the degradation of wooden artefacts.

### *4.3. Physical Properties*

PEG impregnation results in a softening of wood, because the PEG acts as a plasticiser [149,150]. Creep deformation and support of large wooden structures treated with PEG is an issue that requires careful consideration [151]. PEG-impregnated wood exhibits much higher levels of creep compared to sound wood [152]. The easiest way of determining the elastic properties of wood is through the use of quasi-static loading, where the load is applied at a slow rate to avoid dynamic effects. For rare archaeological wood samples, it is better to use cubic wood samples loaded in compression within the elastic limit, allowing the material to be saved [140,153]. However, one problem with such an approach is that the evaluation of data from such experiments can be complicated due to sample inhomogeneity. Creep behaviour of large samples, such as planks, can be more representative, but requires large amounts of material, which may not be available. Ultrasonic testing methods are proving to be a rapid technique for determining elastic properties, but care is needed with the interpretation of results. Resonant ultrasonic spectroscopy (RUS) has been used to determine the dynamic stiffness of wood samples. A comparison of quasi-static compression and RUS performed on recent oak and oak obtained from the Vasa showed that the two techniques were complementary and allowed for the experimental determination of shear moduli and Poisson’s ratios. Creep behaviour is affected by the ambient RH and temperature conditions and is especially sensitive to fluctuations in these conditions. Low MW PEG also has a melting point (17–22 °C) which is close to the ambient temperature of many museums and this can also affect behaviour. The effect of PEG impregnation on cell wall properties was investigated by using nano-indentation [154]. Wood cell walls of sound oak containing PEG were found to exhibit lower stiffness, indentation hardness and higher creep deformations compared to untreated wood. Furthermore, these properties were affected by the presence of moisture, with higher sensitivity found with the PEG-treated samples. These findings were based upon the EMC of the wood samples in total (dry wood mass plus PEG), rather than solely on the dry wood mass. The untreated samples of Vasa wood had slightly higher indentation hardness, stiffness and lower creep deformation compared with the sound wood reference samples. The reason for this was not explained, but is likely to be due to the increased relative lignin content and loss of the plasticising effect of the hemicelluloses, similar to thermal degradation [155]. The observed cell wall softening effect indicates that the PEG is able to plasticise the cell wall both through direct interaction and in the presence of sorbed water, showing that there is no discernable restraining effect of the PEG when located in the cell wall nano-pore space. In waterlogged wood which has been treated with PEG, it is often difficult to determine whether mechanical properties have been changed because of the presence of PEG, or due to post-conservation degradation of the wood. Sound wood which has been impregnated with PEG exhibits a decrease in modulus of elasticity (MOE), work to maximum load, work to proportional limit and compressive strength, properties that are also influenced by the moisture content of the treated wood [156].

### *4.4. Degradation of Consolidated Wood*

Although waterlogged wood exhibits degradation of the holocellulose content especially, further degradation post-conservation remains a possibility and the challenge then is to determine whether this is occurring, why it is occurring and what measures can be adopted to arrest this. The rate of oxygen consumption of a treated wooden artefact is an important determinant of its chemical stability after conservation [157]. Early investigations of this property used sawdust prepared from archaeological wood, but results from such studies can be misleading, since the mechanical process used for the production of sawdust creates free radicals which affect the rate of oxygen consumption. It is important to use solid wood samples to determine the actual rates of oxygen consumption of wooden artefacts that would occur in the museum. A study of different conserved wood samples was unable to identify any single factor that was responsible for the varying rates of oxygen consumption between samples [157]. It was thought that the reaction most likely to be dominant was autooxidation of the wood polymers. Treatment of wood with hot alum solution to mimic the preservation of the Oseberg artefacts significantly increased the oxygen consumption of the treated wood [158], with the presence of iron salts enhancing the oxygen consumption further. The oxygen consumption of the Oseberg samples was found to be consistently higher than that of untreated wood. Treatment of wood with $FeCl_2$ was also found to enhance oxygen consumption markedly, although co-addition of calcium chloride had a slight inhibitory effect. A model study of the effect of deposited sulphur and iron on the degradation of archaeological wood was undertaken by treating balsa wood with reduced iron and sulphur species which concluded that this approach was viable to study the degradation of archaeological samples [47].

The Swedish warship Vasa is a 1200 tonne displacement vessel, which is largely a self-supporting structure, requiring considerable structural integrity of the oak elements. In 2000, salt deposits were discovered on the wood surfaces, which were associated in part with the oxidation of sulphur compounds present in the wood [159]. Sulphur K-edge X-ray absorption near edge structure spectroscopy (XANES) showed that the sulphur in the preserved Vasa wood had oxidation states between 0 and +VI [160], with further oxidation leading to the generation of sulphuric acid/sulphates. Although most of the deposited salts are sulphates, some borates are also present which are derived from the original use of the antimicrobial boric acid/borax combination which was added to the spraying liquid used during the conservation treatment. The large amounts of iron compounds present originate from the different iron objects associated with the ship in service. In-situ, the sulphur and iron compounds in the wood were in a reduced form, due to the anoxic conditions in which the wreck was located. When the hull was reconstructed during the restoration process, a large number of epoxy or zinc-coated iron bolts were used to hold the structure together; many of which are now severely corroded. The iron compounds present in the wood were thought to be capable of catalysing various degradation reactions, including the oxidation of reduced sulphur to sulphuric acid, depolymerisation of cellulose and decomposition of PEG, via Fenton-type reaction pathways [60,81,161,162]. Iron and sulphur particles of various sizes and compositions are present in the surface regions of the wood and present within the cell walls, but there are fewer particles in the wood interior [163]. There is an increase in acidity deeper into the wood, apparently associated with a higher iron to sulphur ratio. Moreover, there is a decrease in the strength of the wood which is thought to be linked to oxygen exposure post-recovery [164]. Remedial action has been attempted by applying wet carbonate/bicarbonate poultices to some areas, or ammonia treatment which is of dubious efficacy [165,166]. However, the application of magnesium and calcium nanoparticles and calcium hydroxide nanoparticles from solvothermal reactions on the Vasa wood samples turned out more effective. The particles penetrated the cell walls and effectively neutralised the existing acids. The excess of their amount was converted into carbonate form, providing an alkaline reservoir that guarantees long-term wood de-acidification [167,168].

Henry VIII's flagship, the Mary Rose, faces similar problems since, for over 400 years, she was resting on a seabed under environmental conditions that promoted the formation of reduced sulphur compounds. Fe K-edge XANES spectra combined with micro-images obtained from S K-edge μ-XANES analysis confirmed the presence of various iron and sulphur compounds at different oxidation levels in the Mary Rose timber, as in the Vasa case, and allowed to study their spatial correlations. To prevent wood degradation by the resulting formation of salts and acids, apart from neutralising the acidic environment by mixtures of soda and bicarbonate and removing iron ions using chelating agents, the application of strontium carbonate nanoparticles is also considered. It could reduce the production of acid formation by reacting directly with sulphur compounds. The tests on small wood samples treated with PEG 200 confirmed the usefulness of this method, which offers hope for appropriate preservation of the endangered valuable shipwrecks [169,170].

Examination of the holocellulose content of wood from the Vasa using size exclusion chromatography showed that the outer 15 mm or so of the wood has a higher MW compared with the interior [160]. It was also found that the outer regions of the wood exhibited a higher tensile strength, which gradually decreased when progressing to the centre of the wood. This result was not expected given that the outer regions of the wood were subject to much higher levels of microbial degradation and also have the highest concentrations of PEG. Iron content was found to increase slightly when going from the exterior to the interior of the wood samples, whereas sulphur content was relatively stable. Significantly higher levels of acetic, formic, glycolic and oxalic acids were found in the interior of the wood, compared to the surface regions. It was noted that depolymerisation of the holocellulose content has not been found in never-dried Vasa wood and other wet-reference waterlogged archaeological wood samples. The oxalic acid is capable of depolymerising holocellulose and can be formed in Fenton-type reactions. Rather than simply considering the iron content it may be that the iron-sulphur ratio is important and it has been suggested that reduced organic sulphur species could function as antioxidants, but this was not observed in the reported study. It was hypothesised that the PEG was exerting some sort of protective effect in the surface regions. Although PEG in the surface layers (0–3 cm) of Vasa wood appeared to be undegraded, further into the wood the PEG exhibited signs of random depolymerisation, which was associated with high iron content. However, samples with higher sulphur to iron ratio did not exhibit degradation to the same extent. This was taken as evidence that the main degradation mechanism was not due to sulphuric acid, but rather an oxidative degradation process catalysed by iron, possibly a Fenton's reaction [61,171]. This hypothesis was tested by reacting holocellulose from undegraded oak and PEG-1500 with hydroxyl radicals generated in a Fenton's system (Fe(II)/$H_2O_2$) [161]. The results obtained with the PEG showed evidence of random chain scission, with alcohol, aldehydic and formate ester end groups, similar to what is observed with degraded PEG from the Vasa. Degradation of the holocellulose was also observed in the model studies and it was noted that exposure of cellulose to Fenton's reagent resulted in the generation of oxalic acid (among other species). This evidence was taken as supporting the hypothesis that Fenton's reactions were occurring within the conserved Vasa wood. Chemical characterisation of degraded waterlogged wood from ancient shipwrecks in the Roman harbour of Pisa showed the presence of high levels of calcium and iron, mostly associated with sulphates [172]. Higher concentrations of iron were associated with a lower degree of crystallinity of cellulose, which was thought to point to iron being a catalyst of random cellulose degradation, again suggesting Fenton's reactions. Studies of the excavated Mary Rose timbers show that the proportion of oxidised sulphur species declines from the surface to the interior of the wood and that the oxidation process was accelerated by the presence of iron [173]. Furthermore, oxidation of sulphur was occurring during the conservation process, in part promoted by the use of PEG solutions which were mediating redox cycling of the iron [113].

Iron sulphides will undergo oxidation reactions in the presence of high levels of humidity to produce hydrated iron sulphates and sulphuric acid, as well as natrojarosite ($NaFe_3(SO_4)_2(OH)_6$), or goethite ($\propto$-FeOOH) [166,174] and the oxidation of iron pyrites to produce sulphuric acid is a very well-known phenomenon associated with mines [55]. The hygroscopic nature of the reaction products encourages further moisture sorption, which promotes the oxidative process. There appears to be a critical RH limit above which iron pyrite oxidation occurs, although there is some uncertainty where this limit lies [55]. The generation of sulphuric acid in conserved marine exhibits results in polysaccharide degradation and depolymerisation, although the lignin and remaining tannins remain relatively intact [175]. By contrast, an oxidative mechanism based upon a putative Fenton's reaction, as proposed in several studies [161,164,176], would be non-discriminatory and would oxidise phenolic as well as polysaccharide content [177–179].

Aerobic oxidation of sulphur can be performed by bacteria, generating sulphuric acid [41,180,181] and acidophilic bacteria, which are capable of oxidising both iron and sulphur, have been identified in the unpreserved timbers of the Mary Rose and this bacterial community undergoes a change in the presence of PEG [113]. In acidic environments, the iron oxidising bacteria *Thiobacillus ferrooxidans* will accelerate the oxidation of $Fe^{2+}$ ions [55]. It is also known that bacteria can degrade PEG [182]. Although bacterial oxidation may be a problem during the often extended period during which conservation takes place, the generally dry environments of museums in which the display of the objects occurs is probably unfavourable to bacterial activity.

There are now many studies underway to identify the best strategy for the removal of iron from the wood [183]. Iron can be removed by the use of chelating agents, such as ethylenediiminobis(2-hydroxy-4-methyl-phenyl)acetic acid (EDMA) [159]. Other suggested methods for iron removal prior to consolidation include electrophoresis [183] and microbial-mediated extraction [181,184]. Although soluble iron salts can be removed from waterlogged wood prior to conservation, iron sulphides are much more intractable [185]. An alternative approach is to accept the continued presence of iron and sulphur compounds, but prevent the ingress of oxygen by the application of a suitable gas-impermeable coating or envelope [55].

However, it has been suggested that removal of iron may not only be unnecessary, but may actually be damaging to the wood. The surface of the Vasa timbers has a higher concentration of iron, a higher pH and the cellulose has a higher molecular weight, compared with the interior of the timbers [176]. The interior of the wood has a lower pH, associated with a decrease in iron content, but an increase in oxalic acid concentration. These results are thought to indicate a reaction between oxalic acid and iron(III)oxides and iron(III)hydroxides to form iron(III)oxalato complexes. The observation that the iron content of the surface of the wood is greater than that of the interior contrasts with some studies [160,186], but is in agreement with others, e.g., [163]. The deposition of iron and sulphur in archaeological marine deposits is a complex process, involving microbiological and chemical mechanisms, depending on local site conditions and may also be different in different wood species [187]. A study of the lignin in the timber of the Vasa used thioacidolysis in combination with gas chromatography-mass spectroscopy in order to determine β-O-4 bonds and syringyl/guaiacyl ratios [188]. No major differences were observed between the lignin of fresh oak samples and that of PEG-treated oak from the Vasa. The lack of any significant degradation of the lignin was taken as evidence that the degradation of the cellulose could not be via an oxidative mechanism involving iron, but rather through the action of sulphuric acid. The lack of tannin in the Vasa oak also indicated that polysaccharide degradation was not mediated by any iron-tannin oxidative process, which is a known mechanism in oak-gall inks.

The rate of corrosion of iron in PEG-400 solutions is dependent upon the concentration of the polymer in the water. The corrosion of iron fasteners in wood can be described in terms of crevice corrosion theory, where one end of the fastener acts as a cathode and the end which is embedded in the wood as an anode. In the presence of oxygen, $Fe^{2+}$ ions are liberated at the anodic end of the fastener, where they react to form iron peroxide (FeOOH). The corrosion of metal fasteners is also affected by the presence of ions such as chloride. The issue of corrosion of iron fixings in archaeological wood that has been treated with PEG has been addressed by the use of corrosion inhibitors [189]. It is known that iron catalyses the oxidation of sulfur in the presence of PEG at 100 °C, but whether this would be an issue at room temperature is uncertain [190]. Oxidation of PEG is accelerated by the presence of hydrogen peroxide and trace metals with the concomitant formation of formic acid, whereas acidic pH promotes the generation of acetaldehyde and acetic acid [191]. PEG is known to strongly bind to iron oxide nanoparticles [192].

A high level of degradation of wood, evidenced by low levels of polysaccharide and extensive lignin oxidation was found in alum-treated wood samples from the Oseberg find, whereas the untreated wood from the timbers of the ship was found to be in good condition [67,95]. A combination of dissolution and derivatization was employed to study the chemical composition of wood in the Oseberg collection, using NMR, gel permeation chromatography (GPC) and pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC-MS) [67]. The study showed that there was an increase in the carboxylic group content of the lignin, an almost total loss of hemicelluloses and significant cellulose depolymerisation, as well as the presence of monomeric sugars in the alum-treated samples. Lignin oxidation products include vanillin, syringaldehyde and syringic and vanillic carboxylic acids, found at much higher levels than encountered in sound wood. The main polysaccharide degradation products are composed of anhydrosugars. The alum-treated woods have been slowly degrading since the time of treatment and are now extremely fragile. The various iron items associated with the finds have also been corroded.

Other techniques for examining the extent of degradation of post-treated wood include evolved gas analysis mass spectrometry (EGA-MS) and a pyrolysis method coupled with gas chromatography and mass spectrometry with in situ silylation (Py(HMDS)-GC/MS), which appear promising providing more detailed information about both the degraded wood and the consolidant [193].

## 5. What Research Has Been Performed and Future Perspectives

Since polyethylene glycol has turned out to be detrimental to wooden artefacts in the long term, a need to find a new, more reliable alternative to preserve newly excavated waterlogged wooden objects has emerged. There is also an urgent necessity to search for solutions that would enable re-conserving the fragile artefacts degraded by the previous treatment (such as Viking artefacts from the Oseberg find or the Vasa ship), effectively strengthening their structure and maintaining them for posterity.

There are three different approaches to these problems. One of them is biomimetics, based on the idea of learning from nature and employing the solutions used and proven effective in nature. In the case of wood conservation, it involves the application of natural materials with hierarchical structure and structural functionalities such as natural polymers (polysaccharides, proteins and their derivatives) to reinforce the degraded wood tissue and simultaneously provide it with stability and flexibility. They are non-toxic, renewable and reduce environmental impact, and are stated to be a “green” alternative to polyethylene glycol. Another approach is to use synthetic polymers with structural properties that mimic natural materials but are much more durable. Finally, the third way is to develop multi-component conservation systems tailored to multiple needs of wooden objects, e.g., providing simultaneous consolidation of the wooden tissue, protection against biodegradation and deacidification.

### *5.1. Sugars and Sugar Alcohols*

Sugars have been tried for wood preservation since the early 1900s. They can effectively protect wood against decay and reduce wood shrinkage and swelling. However, the treated wood becomes damp and sticky under humid conditions [194]. Since they are cheap, non-corrosive, non-toxic, non-volatile, easily soluble in water (which enables reversibility of the treatment by soaking/rinsing with water) and compatible with the size of the pores in the wood, they also found application in the conservation of waterlogged wooden artefacts in the early 1970s. Since that time, their use has been developed and thoroughly studied [97,195].

#### 5.1.1. Sucrose

Sucrose (a disaccharide composed of glucose and fructose) was the first sugar applied for the consolidation of waterlogged wood, including small laboratory samples and large artefacts such as boats and ships [97,195,196]. The impregnation procedure starts with soaking wood pieces in a 5% or 10% aqueous sucrose solution. The concentration is incrementally increased by 5% or 10% until the object reaches equilibrium with the previous solution (or in one- or two-week intervals) [97,126,195]. To increase the stabilisation effectiveness, freeze-drying is suggested following the impregnation. There are two sucrose methods: "cold" at room temperature and "warm" when the solution is heated up to 60 °C. The "cold" method is considered the cheapest conservation treatment for large artefacts and is still in use. In contrast, the "warm" method is not recommended since it often results in the decomposition of sucrose into a non-crystallisable monosaccharide mixture that decreases its consolidation effectiveness [97]. Stabilisation results of the treatment are relatively satisfactory—depending on the wood species and the degree of wood degradation, ASE reaches 81–100% after freeze-drying and 47–98% after air-drying (average ASE is about 75%—laboratory tests on small samples) [126,195,197]. However, highly degraded wood tends to warp and collapse due to the treatment and cannot be stabilised sufficiently. In this case, for small artefacts, post-impregnation freeze-drying can increase the treatment effectiveness, but for larger objects, PEG-treatment is recommended instead. In turn, the sucrose method is mainly recommended for bigger and less delicate artefacts for economic reasons [196].

Sucrose can effectively penetrate wood tissue and crystallise within the cell lumina (its penetration capabilities are similar to PEG 300 or 400). It can also bulk the cell walls due to the small size of its molecules. As a result, it can effectively preserve the shape of individual cells. Sucrose presumably interacts with hydroxyl groups of the remaining cellulose and other wood polymers, thus reinforcing the cell walls. It was stated by the author that the reduction in hygroscopicity was due to the blocking of the wood hydroxyl groups [195]. However, since sucrose contains many OH groups, this would not provide an explanation; moreover, the role that OH group concentration has to play in determining sorption properties in wood is not fully understood [155]. Rather, the reduction in hygroscopicity can be attributed to the extra weight due to the added sucrose plus the bulking effect of the sucrose in the pore space of the wood, which is then no longer available for water molecules.

The aesthetic appearance of sucrose-treated wood is generally acceptable [195]. Sometimes the wood darkens, and white crystals or a brown sticky film appear on its surface [126,197]—the latter results from the degradation of the conservation solution by microorganisms [126]. Sucrose solutions are highly susceptible to microbial attack and prone to fermentation, losing their conservation effectiveness. Therefore, the addition of an efficient biocide and careful monitoring of the biocide concentration during the whole impregnation process is necessary [97,126,195,196]. Additionally, the pH of the solution should be adjusted to 7–9, and the bath temperature should not exceed a temperature of 60 °C [97].

The sucrose method also has other drawbacks. This sugar undergoes hydrolysis over time and reabsorbs moisture. Under high humidity conditions exceeding 70–80%, it can leach out from wood, which leads to unaesthetic crystallised deposits on the wood surface and poses a threat of disintegration to unprotected wood due to swelling and shrinkage under humidity changes [97,126,195,197]. Additionally, the treated artefacts require protection against rodents and insects [97,195].

One of the methods to employ sugars in waterlogged wood conservation and eliminate the flaws of sucrose is the application of non-reactive sugars that cannot undergo hydrolysis, such as sucralose, trehalose or sugar alcohols: lactitol, mannitol, sorbitol, xylitol (or mixtures thereof).

#### 5.1.2. Sucralose

Sucralose (a disaccharide composed of 1,6-dichloro-1,6-dideoxyfructose and 4-chloro-4-deoxygalactose) is relatively unreactive compared to sucrose due to the replacement of three hydroxyl groups with chlorine atoms. As confirmed by Kennedy and Pennington [197], its effectiveness in stabilising waterlogged wood dimensions is comparable to sucralose. The advantage of using this sugar is its long-term stability and better performance at lower concentrations. The impregnation of chemically degraded white birch tongue depressors with 60% sucralose solution (started at 15% and increased by 15% each week) followed by air-drying resulted in the ASE of 63.2% (for sucrose, it was 59%). However, the treated samples were warped and twisted to some degree (which was not seen for samples treated with sucrose and trehalose). This probably results from the substitution of three hydroxyls with chlorine atoms in the sugar molecule that provides sucralose with its stability but also limits its reactivity with wood polymers, thus reducing its reinforcing abilities. On the other hand, the stabilisation effectiveness of sucralose is high. This suggests that the mechanism of stabilisation is different than for sucrose or trehalose and that hydrogen bonding does not play the main role in it.

Considering twisting and warping observed for thin samples, the method is not yet recommended for conservation practice until more knowledge is gained on the effect of sucralose on the structure and mechanical strength of treated wood. It is also worth mentioning that the use of aqueous solutions of sucralose is limited by its solubility. At 60% ($w/v$), sucralose solution is saturated, so it is impossible to use higher concentrations without heating the solution [197].

#### 5.1.3. Trehalose

Trehalose is a disaccharide composed of two glucose units joined by a 1–1 alpha bond. Similarly to sucrose, it is relatively unreactive; however, its anhydrous form readily regains moisture to form the dihydrate. Impregnation with trehalose is considered a viable method for waterlogged wood conservation. It is much faster, safer and less expensive than other methods, completely reversible and appropriate even for heavily degraded wood [97,197]. It provides long-term and spectacular stabilisation effects with cross-sectional wood shrinkage below 2% (the ASE values for different wood samples ranged between 86.2 and 98.6%) [97,197–199]. The method, instead of slow air-drying or freeze-drying, uses fast forced air-drying. This is possible because large amounts of trehalose crystallise inside wood tissue immediately after impregnation. The crystallisation removes about 11% of water, turning it into crystal water in the trehalose dihydrate that fills wood tissue. This provides a stabilisation effect to the degraded structure before the actual drying begins. The trehalose crystals prevent the collapse of the cell walls, thus protecting wood against shrinkage, distortion and cracking. Because the strengthening happens first, fast-drying can be applied as the next step, which reduces the conservation time and costs without losing the stabilisation effectiveness [97].

Two types of trehalose methods are used: “cold” and “warm”. The “cold” method is performed at an ambient temperature, with maximum trehalose concentration not exceeding 41%, which is not enough for efficient stabilisation of highly degraded wood. Therefore, this method is recommended for low and medium degraded artefacts. The “warm” method uses higher temperatures (up to 85%) and much higher trehalose concentration (up to about 90%), usually using a stepwise approach as in the methods mentioned above. It is the fastest among all conservation methods available and suitable for wood at all levels of degradation [97].

Trehalose-treated samples have lower hygroscopicity compared to untreated wood (3.9–4.9% vs. 6.9–7.5% for untreated wood) [199]. Their mechanical properties are generally improved, including the modulus of elasticity and the maximum load of samples in the bending test; however, the samples are more brittle than treated with xylitol [199,200]. The treated wood is often slightly darker in colour; its surface can be sometimes covered with a varnish-like coating or crystalline deposits, which can be easily removed with a damp tissue or gentle brushing [12,197,198]. It was shown that sugar crystals fill the cell lumina of fibres and parenchyma cells, leaving the vessels’ lumina empty [198].

### 5.1.4. Lactitol

Lactitol is chemically more stable and less hygroscopic than sucrose. It is resistant to higher temperatures and alkaline conditions, less susceptible to microbial attack and fermentation, and can be easily removed by dissolving with water providing a reversible treatment. Lactitol-treated wood is not attacked by termites [97].

Similarly to the sucrose and trehalose treatments, there are two methods of wood impregnation using pure lactitol: "cold" and "warm". The "cold" method is performed at an ambient temperature, with lactitol concentration up to 50–55%. The "warm" impregnation is faster than the "cold" one. It involves higher temperatures (between 50 °C and 80–85 °C), and the concentration of lactitol is limited to 75% at 50 °C, and 85% at 80 °C. Due to the concentration limit, the "cold" method is not suitable for the conservation of highly degraded wood, while the "warm" method is appropriate for wood of all degradation types. It must be remembered that at ambient temperature, pure lactitol tends to crystallise into lactitol trihydrate with large crystals, which would damage the fragile structure of degraded wood. Therefore, to avoid it, wood treated with this sugar has to be dried at 50 °C to promote the formation of much smaller and harmless lactitol dihydrate crystals and provide wood with the expected stabilisation effect [97].

For economic reasons, wood impregnation with a mixture of lactitol and 10% trehalose was proposed: the addition of trehalose prevents the formation of lactitol trihydrate crystals during drying, therefore more cost-efficient air-drying instead of drying at 50 °C can be used. Conservation with this method can be performed at both ambient temperature or using temperature in the range of 50 °C to 80 (85) °C (maximum lactitol concentration at 50 °C is 80% and about 90% at 85 °C). The former method is suitable for low and medium degraded wood, while the latter is applicable for all woods despite the degree of degradation [97]. This method effectively reduces wood shrinkage upon drying (cross-sectional ASE for the treated subfossil waterlogged Scots pine samples was 95%, and for waterlogged oak and beech specimens, it was 91–109%) [131,142,201]. It also significantly decreases wood EMC and sorption hysteresis compared to PEG-treated wood. At high air relative humidity, no abnormal increase in equilibrium moisture content (EMC) is observed like for PEG-treated wood, which increases wood safety when exhibited [142]. The method increases the elastic behaviour of treated wood while the loss factor remains unchanged. However, the increased stiffness of the treated wood together with the reduced strength of highly degraded wood, may pose a risk to the artefact's integrity. Therefore, the treatment is generally recommended mainly for small and medium-size objects with a low to moderate degree of degradation [202].

### 5.1.5. Mannitol and Sorbitol

Mannitol and sorbitol were used to impregnate oak samples from the Mary Rose as a potential alternative to trehalose treatment. The samples were soaked in 5, 10 and 20% solutions of individual sugars for one week and then freeze-dried. The best stabilisation effects were obtained for 20% sorbitol solution, resulting in volumetric wood shrinkage of 5.3% and ASE of about 70% (trehalose treatment resulted in 50% ASE). Impregnation with mannitol was less effective, giving wood shrinkage of 12.5% and ASE of 30%; additionally, it left a white crystal covering on the wood surface. The consolidating performance of sorbitol suggests that this method can be more cost-efficient than other sugar-based treatments, shortening the treatment time and reducing the amount of a conservation agent used [12].

Mannitol was also applied to waterlogged wood in a mixture with trehalose. The stabilisation effects were similar to those obtained using lactitol/trehalose mixture, with ASEcs (cs—cross-sectional) reaching 81–103%. Under typical exhibition conditions (RH of 50% and the temperature of 18 °C), the treated wood absorbed less water than wood untreated or treated with lactitol/trehalose mixture [131,201].

#### 5.1.6. Xylitol

Xylitol treatment was tried on chemically degraded wooden tongue depressors. The concentration of 40–60% ($w/v$) effectively reduced wood shrinkage (volumetric ASE of 103–106%) without altering wood hygroscopicity and improved its mechanical properties (increasing the maximum load of samples in the bending test). However, the treated wood was prone to fungal degradation. The treatment was more effective than trehalose and lactitol impregnation performed on similar samples [199].

Although the tested sugars generally performed well and some of them have also been applied in conservation practice, extensive research is still required on their long-term stability and the properties of the treated wood before these methods could be proposed as a safer alternative to PEG treatment.

### *5.2. Proteins*

Proteins are molecules that, inter alia, provide structure to animal cells and organisms. Therefore, they can be considered as potentially useful also for the stabilisation of degraded waterlogged wood.

Proteins have been tried for wood conservation since the beginning of the 2000s. The most promising results were obtained using feather keratin. Keratin belongs to fibrous structural proteins known as scleroproteins and is the main structural component of vertebrate epidermis, hair, nails, horns, feathers, claws, hooves. It is insoluble in water and organic solvents. To apply keratin as a conservation agent, a stable solution is required; therefore, it is usually hydrolysed (using sodium hydroxide) before application on wood. Keratin reduces the surface tension of aqueous solutions. Its pH is 6–7 [203–205].

The best stabilisation results were obtained with hydrolysed duck feather keratin at a final concentration between 30 and 40% (impregnation carried out by stepwise increased concentration, similarly to sugar methods). The higher concentration is not recommended due to the excessive wood swelling leading to its cracking [203]. Depending on the wood species and the degree of wood degradation, ASE between 63.6% and 107.7% was obtained. The treatment turned out to be more effective for less degraded wood [198,203–206]. Goose and chicken feather keratin were less effective in wood stabilisation: the anti-shrink efficiency of 90% and 87.2% were obtained, respectively. It was presumably due to their lower crystalline index and the weaker anti-alkali structures compared to duck feather keratin [203]. To integrate keratin and increase the effectiveness of the treatment, the impregnation was further modified by adding a divalent metal salt (magnesium sulfate) at the end. The obtained results were better than without salt, with ASE over 89%, but for highly degraded wood still not satisfactory—ASE was only 72% [198].

The stabilisation mechanism of keratin is different from PEG [207]. Solid keratin substance has a density similar to the density of the cell wall material (about 1569 kg $m^{-3}$). Its molecules are small enough to quickly diffuse into the wooden tissue and penetrate the cell wall. Keratin adsorbs on the middle lamella, thus reinforcing the cell wall structure and preventing its collapse [198,204,205,207,208]. The remaining open-cell lumina allow for potential retreatment of the samples if necessary [198,207]. The reinforcement of the cell wall translates into improved wood mechanical properties—it was shown in a flexural test that the feather keratin treatment recovers anisotropy of waterlogged wood, as well as the correlation between modulus of rupture (MOR) and modulus of elasticity (MOE) [207].

Keratin treatment maintained the wood colour almost unchanged [198,204,206,207]. The antimicrobial activity of the keratin solution ensured its long-term stability without the addition of any biocides; it also protected the treated wood against bacteria (*E. coli*) and moulds (for more than a year at ambient temperature and moisture content) [204,207]. The treatment also increased wood resistance to UV radiation [204].

However, the keratin-treated wood was highly hygroscopic. Its moisture content and level of swelling were considerably higher than that of PEG-treated samples, which poses a risk of cracking to the wooden object under changeable moisture conditions [207].

Since keratin does not have well defined eutectic temperature, it is not suitable as a pretreatment followed by freeze-drying [205]. The results by Fejfer et al. [123] confirm much lower stabilising effectiveness of the keratin treatment combined with freeze-drying (ASEtangential about 56%, ASEradial about 46–48%) compared to air-drying (ASEtangential between 30 and 64%, ASEradial between 45 and 85%).

The results obtained so far point out that although the feather keratin treatment can be considered a promising waterlogged wood consolidation method, it should be improved before it can be proposed for practical use. It is not appropriate for the conservation of heavily degraded waterlogged wood, but may be applied as a bulking or stabilisation agent for better-preserved, non-collapsible wood [205]. Interestingly, the method was effective in the conservation of a fragile archaeological waterlogged polypore (about 2600 years old), found at the Neolithic site of Kitashirakawa in Kyoto, Japan [209]. Further research is needed, e.g., on the influence of keratin molecular mass on its stabilising effectiveness, potential additives to improve consolidation of degraded wood, as well as health and safety aspects of keratin's application [205,208].

Hydrolysed silk fibroin has been tried for waterlogged wood stabilisation, although it effectively reduced wood shrinkage, it turned out to be inapplicable due to the low stability of the solution and its tendency to settle even at a concentration of 10% [204].

### *5.3. Cellulose and Its Derivatives*

Cellulose is an easily available natural linear polysaccharide composed of hundreds or thousands of $\beta(1\rightarrow4)$ linked D-glucose units. It is the most abundant polymer in nature and one of the main components of the wood cell wall, which provides it with strength and rigidity. Therefore, different forms of cellulose and its derivatives seem the obvious choice while looking for a consolidation agent for degraded waterlogged wood.

A 5% aqueous suspension of bacterial nanocellulose (nanospheres) obtained by agroalimentary waste fermentation effectively stabilised dimensions of different waterlogged archaeological hardwoods (ASE of 80–88%), but their effectiveness was more variable for waterlogged softwoods (ASE of 55–94%). The particles penetrated wood tissue, filled most of the cell lumina and formed a compact layer on the cell walls, but their consolidating effects were not satisfactory. The conservation suspension tended to precipitate during impregnation and required constant stirring to prevent this. Despite this, an unaesthetic layer of nanocellulose particles on the wood surface remained after the treatment, but it was relatively easy to remove by gentle brushing. The treatment resulted in yellowing or whitening of wood, which can presumably be avoided by adding an appropriate pigment to the solution. The EMC of the samples remained almost unaltered [210].

Cellulose nanocrystals were less effective than bacterial nanocellulose, giving an ASE in the 37–84% range. They penetrated only about a millimetre inside the wood tissue and coated the cell walls, leaving the cell lumina empty. The impregnation solution turned into gel after a week of treatment, which resulted in the formation of a gel coating on the wood surface (easy to remove by brushing). The colour of the treated samples was similar to the untreated control, and the EMC remained almost unaltered [210].

Wood impregnation with nanocellulose whiskers (rod-like nanoparticles) encountered similar problems with wood penetration and precipitation in the conservation solution. However, it showed that such particles can adhere well to the wood surface and can act as gap-fillers enhancing wood stabilisation [211].

The results of the experiments using different forms of cellulose point to the conclusion that perhaps a better wood stabilisation could be obtained by combining nanoparticles of different shapes—spherical with filamentous ones. This should help fill the voids of different sizes and shapes in the cell walls and create an internal cellulosic network to stabilise the degraded wood. However, the improvement of cellulose penetrability is required first, which could be achieved by adding some surfactants, such as salts or PEG, or by chemical modification of hydroxyl groups present on cellulose particles. Research is also needed to prevent the precipitation or gel formation by nanoparticles in the solution.

It would be highly undesirable to use cellulose whiskers that are produced using sulphuric acid digestion, because the obtained cellulose would be sulphated, and its application as a wood consolidant would result in the same problems we face today with sulphur compounds present in waterlogged artefacts such as Vasa or Mary Rose [210,211].

Crosslinkable cellulose ethers (allyl cellulose, allyl carboxymethyl cellulose, and allyl n-hydroxypropyl cellulose) were also tried for waterlogged wood stabilisation. They were able to penetrate wood samples but only to a limited extent, probably due to the high molecular weight of the ethers or their aggregates present in the conservation solution or due to the limited impregnation time (20 days). The tested cellulose ethers exhibited a high affinity to lignin (the main component of degraded waterlogged wood), but due to crosslinking, the treatment turned out to be irreversible (in contrast to commercial sodium carboxymethyl cellulose, where high reversibility was obtained). Further research is required to improve the effectiveness of this method and evaluate the wood properties treated with cellulose ethers [212]. Klucel (hydroxypropyl cellulose, commonly applied in wood conservation [213]), however, was quite effective in stabilisation of wood dimensions and strengthening its structure, but was also not able to fully penetrate waterlogged wood samples. The EMC of the treated wood was similar to untreated. Optimisation of the conservation process is required, as well as studies on the long-term performance of treated wood [92,214].

Recently, two other cellulose derivatives potentially useful in waterlogged wood conservation have been synthesised and studied: 6-deoxy-6-($\omega$-aminoethyl) amino cellulose AEA-1$'$ and its alkyl derivative 6-deoxy-6-($\omega$-hydroxyethyl) amino cellulose HEA-1$'$. The molecular mass of their monomers is in a range of 3.3–5.5 kDa, and they exhibit a protein-like self-associative behaviour. These properties make them suitable to penetrate the degraded wooden tissue and aggregate inside it into larger structures, thus strengthening it and providing stabilisation. The self-association of the chemicals can be partially reversible, which would facilitate the removal of at least part of the polymer from the wood if necessary. The research on the performance of waterlogged wood treated with amino cellulose is in progress [215].

### *5.4. Lignin and Its Derivatives*

Lignin is a natural polymer composed of cross-linked phenolic precursors. It is the second most abundant polymer in the world and a component of the wood cell wall where it provides structural rigidity. Due to its high chemical and biological resistance, it is often the major ingredient remaining in the degraded waterlogged wood and an object of interest as a potential consolidating material.

Lignin nanoparticles obtained from beech wood by the non-solvent dialysis method were used to consolidate different waterlogged wood species. They exhibited only low to moderate stabilisation effectiveness with an ASE of 51–88%. They precipitated at the bottom of the conservation solution, and despite the constant stirring during impregnation, they deposited on the wood surface. The particles were easy to remove by brushing. However, after drying, they were still present on the surface as a fine brown powder, and the colour of the treated wood changed to dark brown. The penetration ability of lignin nanoparticles was poor (about 1 millimetre inside wood tissue), probably due to their hydrophobicity and a tendency to aggregate. They coated the cell walls and filled the cell lumina in the external parts of the treated samples. The equilibrium moisture content of the treated wood remained almost unchanged. A careful selection of lignin sources could help obtain particle colours that match the colour of the treated wood. The impregnation conditions require changes that prevent the precipitation of lignin nanoparticles and facilitate their penetrability into the wood structure [210].

To increase the potential of interactions with wood polymers, different lignin derivatives were synthesised and applied to waterlogged wood. Lignophenol (a polymeric lignin derivative isolated from wood) showed good stabilisation effectiveness for wood differing in the degree of degradation due to hydrophobisation of the cell walls. It also significantly increased wood hardness in comparison with PEG4000-treated samples [216]. Lignin-like oligomers synthesised from isoeugenol in a 10% ethyl acetate solution fully and evenly penetrated small waterlogged wood samples (1 $cm^3$) and coated the cell walls; this shows the potential of these dehydrogenated polymers as consolidants [217]. An in situ polymerisation of isoeugenol monomers inside waterlogged wood has also been tried. It involved wood impregnation with the isoeugenol monomer via bulk addition, and then adding horseradish peroxidase and $H2O_2$ to start polymerisation reactions. As a result, a polymer structure rich in the chemically stable β-5′ moiety was formed inside the wood tissue, effectively consolidating wood samples so they could be handled and cross-sections for microscopy imaging could be cut out from them [218]. The preliminary results of these protocols are promising and further research on the consolidation ability of isoeugenol and its derivatives and long-term stability of the treated wood is planned [217,218].

Lignin-silicon hybrids obtained by the reaction of allylated lignin with poly(dimethyls iloxane) hydride terminated on both the ends of the silicone chain through a hydrosilylation reaction in the presence of the Karstedt's catalyst were applied to oven-dried waterlogged wood. The impregnation resulted in the increased hydrophobicity and chemical durability of the treated wood. However, the applied chemicals deposited mainly in the external parts of wooden samples, preventing their further penetration into wood tissue. The penetration was also impeded by the steric hindrance of the platinum catalyst necessary in the reaction. The limitations of the proposed conservation method make it hardly applicable for waterlogged wood conservation, but perhaps it could be useful for the consolidation of already dry historical wood. Further study is required to improve the penetrability of the solution and the stabilisation effectiveness of the treatment [219].

### 5.5. Chitosan and Guar

Chitin, a natural mucopolysaccharide consisting of 2-acetamido-2-deoxy-β-D-glucose linked by β(1→4) bonds, is the main component of arthropod exoskeletons. It is the same as cellulose with only a hydroxyl group replaced by an acetamido group. Chitosan is the N-deacetylated derivative of chitin, renewable, biodegradable and non-toxic. Due to its structural functionality, similarity to cellulose, better compatibility with wood than synthetic polymers, and proven antifungal and metal chelating properties, it seems to be a promising multifunctional and "green" consolidant for waterlogged wood conservation [220–223]. The results show that low concentration chitosan solutions (1–2%) can penetrate waterlogged wood tissue (more easily when it is depolymerised) and strengthen it without altering the natural relaxation behaviour of wood, leaving the wood structure open for potential further re-conservation. Chitosan of varying degrees of polymerisation and deacetylation and its tert-butyldimethylsilyl derivative were also tested as potential consolidants for the already dry degraded archaeological wood giving promising results for future application on fragile alum-treated artefacts such as those from the Oseberg finding [224,225]. Further tests are required on the stabilisation effect of chitosan, as well as the long-term stability and other properties of chitosan-treated waterlogged and archaeological wood [211,220,221,225].

Promising results were also obtained for guar gum. Guar gum is an exo-polysaccharide composed of galactose and mannose, known for its thickening and stabilising properties. Tested as a consolidant for waterlogged wood, it exhibited good penetration ability, great compatibility with wood, and strengthening properties even at a low concentration (only 1%), which illustrates its potential in waterlogged wood conservation [221].

An innovative multi-component supramolecular conservation system based on guar and chitosan has been developed to address three primary needs of waterlogged archaeological wooden artefacts: structural instability upon drying, susceptibility to biodegradation and vulnerability to chemical degradation caused by $Fe^{3+}$-catalysed acidification. Guar and chitosan are safe polymers that provide structural support and do not form acidic by-products on degradation. Chitosan has antimicrobial properties and reactive amino groups available for further functionalisation, while guar can be functionalised through the diol unit. Guar was enriched with a boronic acid functionalised viologen derivative that provides it with strong biocidal activity. Chitosan was functionalised with naphthol and catechol (the latter enables metal–ligand interactions with $Fe^{3+}$ ions). To link polymers, the host–guest chemistry of cucurbit [8] uril was employed. As a result, a dynamic spatial polymer network was formed with three parallel functionalities: structural support (chitosan and guar cross-linked by cucurbit [8] uril), removal of $Fe^{3+}$ ions (siderophore activity of catechol) and resistance to biodegradation (chitosan, boronic acid functionalised viologen derivative). The system was tested on degraded waterlogged archaeological oak and was effective in all its three activities (shrinkage reduced to 30% compared to 50% of untreated wood). Although further study on this innovative and reversible system is required, it seems to be a reliable, greener alternative to the methods being in use in the conservation of waterlogged wooden artefacts [226].

### 5.6. Oligoamides

Following the trend of using more “green” compounds, three different water-soluble hydroxylated oligoamides with a chemical structure similar to the main wood polymers were synthesised and tried as consolidants for waterlogged wood: polyethylene-L-tartaramide, polyethylene-D(+)-glucaramide, polyethylene-$\alpha$,$\alpha$-trehaluronamide. They showed high affinity to lignin, usually the main polymer that remains in degraded wood, and good penetrability into wood tissue (much better than cellulose derivatives). They reduced hygroscopicity of the treated wood and reduced wood shrinkage compared to untreated samples (volumetric shrinkage was between 39 and 49% compared to 60% for untreated wood, and the ASE was 18–35%). Although the dimensional stabilisation by oligoamides was beyond the level required by conservation practice (ASE of at least 75%), the chemicals are considered of great interest for the development of the new generation of consolidants waterlogged wood [227].

Experiments that involved four different oligoamides (oligo ethylene-L-tartaramide, oligo esamethylene-L-tartaramide and copolymer between ethylenediamine, adipic and tartaric acids, and allyl $\alpha$,$\alpha'$-trehalose/vinyl alcohol copolymer) applied on waterlogged oak and ash showed their high affinity for lignin, good penetration into wood tissue and effectiveness in the reduction in wood shrinkage upon drying compared to untreated samples. The effectiveness was higher for more degraded ash samples due to its higher porosity, and thus higher permeability for high-molecular consolidants. Oligoamides exhibited higher reversibility than allyl $\alpha$,$\alpha'$-trehalose/vinyl alcohol copolymer [228].

### 5.7. Other Natural Compounds

There is an extensive list of natural substances that have been used to consolidate waterlogged wood. Wood tar and waxes are some of the examples used in the past to protect wooden objects. Beeswax, carnauba wax and paraffin are sometimes still used for small and fragile artefacts and wood/metal composites [127]. The application of other natural compounds is described below.

Colophony is a natural resin obtained from pines and other conifers. It consists mainly of abietic acid (silvic acid), and is commonly used in adhesives, varnishes and sealing wax production. Rosin is chemically modified (esterified) colophony (ester of pentaerythritol).

Colophony and Rosin are applied to waterlogged wood as acetone solutions. This enables the quick distribution of the consolidant inside the wood tissue and reduces drying time. Retention of consolidants is high (weight percent gain at least 70% *w*/*w*, higher for colophony than its derivatives—a linear relationship was found between the level of retention and molecular weight of consolidants), and the more porous the wood is, the higher the consolidant retention. The consolidants easily penetrate wood tissue. They do not fill all the cell lumina (the largest remained empty) but efficiently encrust the cell wall, thus increasing its volume and strengthening the wood structure. As a result, the shape and dimensions of the treated samples are well maintained, no splitting or cracking is observed. To obtain a more natural colour of treated wood (not too dark), McKerrell et al. proposed pre-treatment with dilute hydrochloric acid followed by impregnation with rosin in acetone solution [229]. The equilibrium moisture content of the colophony-treated wood remains comparable to that of untreated wood, but treatment with Rosin significantly reduces it. This helps to maintain a good stabilisation effect despite humidity variations and reduces the risk of fungal infestation. Due to the larger size of the molecules and chemical reactivity, Rosin seems more effective in consolidating severely degraded wood. The treatment is appropriate for both softwoods and hardwoods [92,128,229–231]. However, it must be remembered that, similarly to PEG, rosin has a significant plasticising effect on wood. Therefore it seems more suitable for smaller artefacts that do not have a load-bearing function. As a natural substance, rosin is susceptible to ageing, and becomes more brittle in time [202]. The reversibility of colophony/rosin treatment is questionable [58].

Following the trend of searching for bioinspired consolidation materials, recently a new polyhydroxylated monomer was synthesised from $\alpha$-pinene (a terpene derived from coniferous trees) and used to obtain a TPA5 polymer through free radical polymerisation. The polymer has an elongated shape, a low molar mass (about 4.5 kDa on average) and a great potential for hydrogen bonding (e.g., with wood polymers and other polymers), which makes it potentially interesting as a consolidant for waterlogged wood [232].

### *5.8. Halloysite Nanotubes*

Another approach is the application of Halloysite nanotubes. Halloysite is a natural aluminosilicate clay mineral. Its dominant form is hollow nanotubes (small cylinders) about 0.5–10 µm long, with an inner diameter of 10−60 nm and an outer diameter of 50–300 nm. Nanotubes are made of aluminosilicate sheets rolled up into a layered structure, with an interlayer distance of 0.6 or 1 nm depending on the hydration state of the mineral. The external surface is composed mainly of $SiO_2$ and negatively charged, while the inner surface, consisting of $Al_2O_3$, is charged positively. This allows for the selective modification of inner and outer surfaces with different substances, making Halloysite nanotubes suitable carriers for the sustained release of active molecules and reinforcing fillers for various polymers. Hence the idea to try them as consolidants for waterlogged wood [233–235].

Halloysite nanotubes were mixed with beeswax in acetone and used to consolidate waterlogged wood samples (Pinus pinaster Aiton) from the ship Chretienne C (II century, BC) discovered off the coast of Provence. The samples were first dehydrated in acetone, then immersed in the consolidation mixture for three days under magnetic stirring and air-dried. The consolidation resulted in reduced volumetric shrinkage of wood samples from 40.6% for untreated to 6.2% for treated ones, which gives the ASE value of about 85%. The addition of Halloysite nanotubes also enhanced the thermal stability and mechanical properties of beeswax, which makes the applied mixture a potential consolidant for waterlogged wood [236].

The idea was further developed into a new consolidation system—a Pickering emulsion based on Halloysite nanotubes with paraffin wax microparticles as the inner phase of the oil-in-water droplets. Treatment with this organic/inorganic hybrid system reduced volumetric shrinkage of waterlogged wood from the Chretienne C ship from 40% to less than 5% (ASE of 87.5%) by filling the cell lumina and coating the cell walls, thus preventing their collapse upon drying. It also enhanced wood mechanical properties such as stiffness and flexural strength (the elastic modulus and stress at the breaking point increased to the order of magnitude of sound wood of the same species) while it reduced wood elongation capability by 50%. The colour of the treated samples was similar to untreated ones. The results obtained confirm that the organic/inorganic hybrid system composed of Halloysite nanotubes and wax can potentially be used as a consolidant for waterlogged wooden artefacts. It is worth mentioning that the proposed conservation method is environmentally friendly since the components applied are natural and non-toxic, and water was the only solvent used. It then can be scaled up to the requirements necessary for the treatment of large wooden objects [237].

Halloysite nanotubes were also tried for waterlogged wood consolidation in combination with 50% acetone solutions of esterified colophony (Rosin) (wood samples from the above-mentioned ship, an analogical impregnation protocol), and as a composite with Pluronic F108 (Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol). The effectiveness of the former method was lower than that of the Halloysite nanotubes/wax or beeswax mixtures, reaching ASE between 36 and 65% (volumetric wood shrinkage after the treatment was 14–26% compared to 40% for untreated wood). In the latter method, the mixture could only effectively penetrate the wood cell lumina [238,239].

Halloysite was employed as a component of a multifunctional hybrid system for simultaneous consolidation, deacidification and long-term protection of waterlogged wood from chemical degradation under acidic conditions. Wood samples were impregnated in aqueous dispersions of PEG1500 and Halloysite nanotubes loaded with calcium hydroxide as described above. The conservation system successfully penetrated wood tissue, filled the cell lumina and reduced wood porosity, which resulted in significant enhancement of wood mechanical properties (flexural strength and rigidity) in comparison to PEG-treated wood. The treated samples were robust and resistant to crushing. The sustained release of $Ca(OH)_2$ from the Halloysite lumen proved effective in neutralising the acidifying effect of PEG degradation by-products measured on the wood surface for 12 months. Moreover, it protected lignin against chemical degradation during artificial ageing under an acidic atmosphere. This makes this "green" conservation system potentially useful also for re-conservation of acidified artefacts previously treated with PEG or alum [240].

There is still much research needed before clay nanotubes can be proposed as a standard conservation method. Information about the anti-shrink efficiency of the method for wood with differing degrees of degradation, its long-term durability, reversibility or retreatability is required, as well as more data about characteristics of the treated wood, including its moisture and aesthetic properties or resistance to biodegradation. However, Halloysite nanotubes seem to have great potential for waterlogged wood conservation—their ability to improve thermo-mechanical performance of various polymers and the possibility for encapsulation of additional molecules of specific functionality (e.g., antifungal, hydrophobising, deacidifying) make them a perfect compound for multi-functional organic/inorganic hybrid systems tailored to the needs of waterlogged wood.

### *5.9. Organosilicon Compounds*

Organosilicon compounds can be defined as organometallic compounds containing carbon–silicon bonds. They can be synthesised into various molecular structures, starting with the simplest silanes, through linear or branched siloxanes, to polyhedral silsesquioxanes. Due to their unique chemical reactivity and many potential functionalities, high thermal stability and resistance to external factors, they have been commonly used in many industry sectors, including the wood industry, mainly as adhesives, coatings, sealants and adjuvants. The most common silicon derivatives are organofunctional alkoxysilanes. Owing to the presence of alkoxy groups, alkoxysilanes can polymerise in the sol–gel process. It proceeds through a series of consecutive hydrolysis and polycondensation reactions, leading to the formation of a spatial polymer network. The presence of functional groups provides them with additional specific functionalities [241–243].

In the conservation practice, organosilicon compounds have been sporadically used for waterlogged wood conservation since 1965, when a mixture of PEG, boric acid, borax, and methylpolysiloxane was sprayed over the hull of the Vasa warship. Attempts to use tetraethyl orthosilicate (TEOS) or methacrylate-dimethylsiloxane oligomers for waterlogged wood consolidation were also made [127]. The first fully organosilicon-based conservation method was proposed by C. W. Smith in 1993 and then patented by Klosowski and Smith and Klosowski et al. It employed a primary silicon polymer (silicon oil, polydimethylsiloxane) and a cross-linker (methyltrimethoxysilane, MTMOS) for impregnation of acetone dehydrated wood followed by the addition of a catalyst to ensure the formation of a strengthening three-dimensional polymer network inside the wood structure [126,244,245]. The method was used to consolidate several waterlogged marine and freshwater artefacts made of wood, bone, ceramic and textiles, including objects from the sunken city of Port Royal, Jamaica, the Uluburun shipwreck and the French shipwreck La Belle. The treatment, however fast and effective for preventing wood shrinkage (the ASE of about 82–90%) and discolouration, is irreversible, and the chemicals used are volatile and toxic. The long-term stability of the treated objects has not been confirmed. The method is suggested to be practical for conserving small waterlogged wooden artefacts [126]. Modification of the method by exchange of acetone with turpentine after wood dehydration and exposure of dry impregnated wood to MTMOS vapours instead of its immersion in the liquid silane improved penetrability of the consolidation mixture inside the wood. The treated samples retained their natural colour and dimensions; no shrinkage or collapse was observed [245]. The treatment did not alter wood mechanical properties, and its stabilising effect seems to result from high retention of the consolidant [202].

The results of more recent research show that the conservation method using organosilicon compounds can be simplified and include the following steps: wood dehydration in ethanol followed by soaking impregnation with an ethanol solution of a selected organosilicon without any catalysts, and finally, slow air-drying [246,247]. Among several tested chemicals, the most effective in stabilising the dimensions of highly degraded (loss of wood substance ca. 70–80%) elmwood were: (3-mercaptopropyl)trimethoxysilane (MPTMS, ASE ca. 98%), (3-aminopropyl)triethoxysilane (APTES, ASE ca. 91%), 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (BAPTMDS, ASE ca. 91%), 1,3-Bis-[(diethylamino)-3-(propoxy)propan-2-ol]-1,1,3,3-tetramethyldisiloxane (BDEPPTMDS, ASE ca. 90%), 3-(Polyethoxypropyl)1,1,1,3,5,5,5-heptamethyltrisiloxane hydroxyl-terminated (PEGHMTS, ASE ca. 89%), methyltrimethoxysilane (MTMS, ASE ca. 81%) [247]. MTMS turned out to be quite a versatile consolidant, effective for wood differing in the degree of degradation: applied on highly degraded elmwood (with the loss of wood substance (LWS) in the range of 70–64%), it gave the ASE values of 70–95% (higher stabilisation effect was observed for less degraded samples); when used for highly degraded oak sapwood (with LWS ca. 81%), the ASE reached 97–103% (higher values while the oscillating-pressure method was used instead of simple soaking); the lower stabilising effect was observed for better preserved oak heartwood (LWS ca. 25% for outer and 8% for the inner part, respectively) with the ASE of about 68% and 61%, respectively. The lower effectiveness for oak heartwood resulted from much lower permeability of well-preserved wood tissue (the observed weight percent gain after the treatment was about 4 times lower for heartwood than for heavily decayed sapwood) [35,246]. Although at this stage it is impossible to state what makes the organosilicon an effective wood consolidant, it can be concluded that the most effective were the chemicals with small molecules able to penetrate wood tissue easily and potentially bulk the cell wall, and those with other reactive groups allowing for extra interactions with wood polymers. SEM images of the treated wood revealed that organosilicons with smaller molecules (MTMS, MPTES, APTES) coat the cell walls or maybe even encrust them, leaving the cell lumina empty, while larger molecules (BAPTMDS, BDEPPTMDS) both coat the cell walls and fill smaller cell lumina, which suggests different stabilisation mechanisms [35,247,248]. Surface area and porosity measurements confirmed that MTMS could bulk the cell wall of the treated wood, thus stabilising the wood microstructure [91]. Strong chemical interactions between alkoxy groups in alkoxysilanes (MTMS, MPTES) and hydroxyls in wood polymers or weaker hydrogen bonding between amino groups in BAPTMDS and wood, confirmed by Fourier-transform infrared spectroscopy (FT-IR), contribute to the stabilising effect [249].

Apart from amino silicons, the chemicals reduced wood hygroscopicity, which would prevent further potential wood dimensional changes upon changeable moisture conditions [91,247,250,251]. The treatment with MTMS enhanced wood resistance against the brown-rot fungus *Coniophora puteana*, but gave no protection against moulds [251]. Experiments with soaking of the treated wood in 50% ethanol for two weeks showed that the treatment with siloxanes and amino silanes could be reversible, which is in line with conservation ethics. On the other hand, although the impregnation with hydrophobic alkoxysilanes turned out to be more durable, the chemicals left the cell lumina empty, which potentially allows for further wood re-conservation; the method can then be considered as retreatable [247]. More research on the method is necessary to establish the actual stabilising mechanism, the effect of the treatment on the wood mechanical properties, and the long term stability of the treated wood.

Organosilicon compounds were also used as components in different conservation mixtures used for already dry wood. Methyltrimethoxysilane was successfully applied for re-conservation of PEG-treated sabot, effectively preserving the original dimensions of the object, reducing the feeling of wet and greasy surface, but changing the wood colour to a much lighter hue [252]. New organic/inorganic multi-functional hybrid systems composed of propylene glycol-modified silane, alkaline nanoparticles ($Ca(OH)_2$), and one of the following compounds: 3-aminopropyl triethoxysilane, trimethylamine, and polydimethylsiloxane hydroxy-terminated proved to be effective deacidifying consolidants in the one-step conservation of the fragile alum-treated wood from the Oseberg find. Application of silane monomer and nanoparticles allowed for efficient penetration of the chemical into the wood structure, where they underwent polymerisation into a three-dimensional network together with lignin that remained in the wood. The treatment increased the robustness and pH of wood without any distortions or shrinkage; it also effectively consolidated wood, reducing its powdering upon handling [253].

### *5.10. Other Polymers*

Several different polymers have been applied to consolidate waterlogged wooden artefacts, such as hydroxyethyl methacrylate, vinyl acetate, poly(vinyl chloride) or poly(acrylamide). However, they were ineffective mainly due to poor penetration into the wood structure resulting in its insufficient stabilisation, shrinkage and excessive cracking [92,101,127,128].

Some other polymers were more promising. One of the examples is phenol-formaldehyde. It has a lignin-like structure but higher resistance to degradation. Although its curing process is irreversible, there was an attempt to use it for the consolidation of wood from waterlogged pillars excavated in China (the remains of an ancient village). Wood was dehydrated in methanol and pre-treated with 2% oxalic acid to reverse its discolouration by bacteria. Then the proper treatment with 20% neutral phenol-formaldehyde in methanol was applied, which prevented wood shrinkage and warping upon drying, increased its strength and stabilised the colour. The treated wood structure remained porous, which, despite the irreversibility of the applied treatment, allows further re-conservation if necessary [254]. An acid-catalysed phenol-formaldehyde (novolac) has also been investigated as a potential consolidant for already dry, extremely fragile alum-treated objects from the Oseberg find. It was shown to thoroughly penetrate wood tissue and undergo in situ polymerisation inside it (at very low pH). The structure of the treated wood was strengthened and remained open owing to phase separation while using acid-catalysed novolacs (based-catalysed resols did not give such good results), allowing re-treatment. The cured consolidant is resistant to acids and ageing. However, the treatment can be inappropriate for highly degraded alum-filled artefacts because the pre-polymer mixture dissolves alum crystals risking disintegration of the wooden object. Further research on larger wood pieces is necessary to assess the actual usefulness of the method, as well as finding more safe solvents to prevent the dissolution of alum crystals during the treatment [211,255].

Melamine formaldehyde is a thermosetting resin of good chemical stability, composed of melamine rings terminated with numerous hydroxyl groups derived from formaldehyde. The small size of its molecules (about 5 Å) and solubility in water allow for its penetration into wood tissue [211,256]. A waterlogged wood consolidation method (also known as the Kauramin method) using melamine formaldehyde has been developed in Germany. It uses low-molecular (400 to 700 g/mol) polymer with low viscosity. The impregnation is carried out under ambient conditions, at a pH of about 7. Depending on the size and the degree of wood degradation, it can take a few weeks up to one year. After impregnation, the treated wood is oven-dried at 50 °C for 7 to 14 days to ensure resin polymerisation. Compared to PEG-treatment, the Kauramin method is shorter, and the treated artefact is low in weight. However, due to the cross-linkage of the resin upon drying, the treatment is irreversible, which means that the treated object becomes a polymer composite without any possibilities for retreatment [202,211,256,257].

The melamine formaldehyde method provides an excellent dimensional stabilisation, and it is suitable for heavily degraded waterlogged wood. Sometimes deep cross-grain cracks may occur in the treated wood [256,257]. To prevent the formation of an unaesthetic polymer coating on the wood surface, the polymerisation rate of Kauramin should be controlled by careful monitoring of the pH and the turbidity of the solution [256,258]. The changes in wood colour (a much lighter tone) may appear due to wood bleaching by the release of formaldehyde during the thermosetting. To improve wood colour and appearance after the treatment, the wood surface should be treated with wax and darkened with natural oils [202,211,257,259]. It is recommended to add urea to the Kauramin solution to decrease the hazardous effect of free formaldehyde on human health. Additionally, urea increases the penetrability of the solution into wood tissue by decreasing its viscosity [256]. Kauramin imparts high strength to very fragile, highly degraded waterlogged wood and limits its hygroscopicity [259]. Similarly to other curing resins, it contributes significantly to the elastic properties of the treated wood, but only slightly to its viscous behaviour, which results from its polymerisation within wood tissue forming a stable composite material [202]. The addition of triethylene glycol to the melamine-formaldehyde solution increases the flexibility of the treated wood [256].

It must be noted that consolidation of waterlogged wood using melamine-formaldehyde is inconsistent with conservation ethics because of its irreversibility. Despite this, conservators sometimes choose this method due to the particular requirements of the object or exhibition conditions. The Yenikapi shipwreck conservation project in Istanbul, Turkey, is such an example. The conservation method applied was expected to be cost-effective regarding time and resources, and provide a consolidation effectiveness good enough to preserve heavily degraded wooden wrecks and enable their exhibition under uncontrolled environmental conditions. As a result, the Kauramin method was employed as the primary conservation treatment for highly deteriorated elements, in some cases in combination with PEG impregnation. This enabled the salvage of fragile artefacts that would probably not survive any other treatment procedures [122,256,259]. Similarly, part of the Roman-Germanic Central Museum (RGZM) collection in Mainz, Germany, was treated with this method [256]. Further reporting on the performance of Kauramin-treated artefacts is needed to evaluate the actual effectiveness and safety of this conservation method.

Recently, a new method for waterlogged wood stabilisation has emerged, namely, activators regenerated by electron transfer for atom transfer radical polymerization (ARGET ATRP), which uses reducing agents to continuously reduce a deactivator Cu(II) to an activator species Cu(I). In this case, it employs wood modification with by 2-bromoisobutyryl bromide in $CH_2Cl_2$ to acquire C-Br bonds as initiators, then butyl methacrylate or styrene is introduced into the wood and polymerises there with the use of catalyst ($CuBr_2$), reductant (ascorbic acid) and ligand (N,N,N′,N″,N″-pentamethyldiethylenetriamine) in ethanol. Wood samples are then washed and left for natural air drying. The method results in good dimensional stabilisation of waterlogged wood (ASE of 87.8% for polystyrene and 98.5% for polybutylmethacrylate treatment) without collapse or distortions. The polymerisation takes place within cell walls, leaving the cell lumina empty, which allows for potential future wood re-treatment. The method theoretically has great potential due to the possibility of applying different, less toxic and more effective chemicals to obtain even better consolidation results [260]. It has been revised latterly by using less toxic chemicals, including mercaptoethylamine to functionalise waterlogged wood, quinone-based initiators, ascorbic acid 2-glucoside and glucose as reductants and water as a solvent. They obtained a relatively satisfactory ASE of 77.0–85.1% confirms the stabilising potential of the method [261].

A summary of the most important properties of wood treated with new consolidants is presented in Table 2.

**Table 2.** The effects of different conservation methods on wood properties: "+"—improvement, "-"—negative effect, "ncs"—not changed significantly, " . . . "—not studied; "fd"—freeze-drying, "ad"—air-drying.

| Method | ASE [%] | Appearance | Mechanical Properties | Moisture Properties | Resistance to Fungi | Reversibility | Other |
|---|---|---|---|---|---|---|---|
| | | | | Sugars and sugar alcohols | | | |
| Sucrose [97,126,195,197] | 81–100 (fd), 47–98 (ad) | darker colour, crystalline deposits, a sticky film of wood surface | . . . | + (under RH < 70%] | - | + | cell lumina filled, the cell wall bulked |
| Sucralose [197] | 63 | wood warping and twisting | . . . | . . . | - | + | long-term stability, reduced reactivity with wood polymers |
| Trehalose [97,197–199] | 86–99 | darker colour, crystalline deposits or a coating | + | + | - | + | faster, cheaper and safer than other methods, long-term stabilisation effect, smaller cell lumina filled |
| Lactitol [97,131,142,201] | 91–109 | ncs | + | + | - | + | recommended for small artefacts |
| Mannitol and sorbitol [12] | 70 (sorbitol), 30 (mannitol) | crystalline deposits on the wood surface (mannitol) | . . . | . . . | - | + | sorbitol—more cost- and time-efficient than other sugar methods |
| Xylitol [199] | 103–106 | ncs | + | ncs | - | + | more effective than trehalose and lactitol treatment |
| | | | | Proteins | | | |
| Keratin [204,205,209] | 64–108 | ncs | + | - | + | potential retreatment | more effective for less degraded wood, cell lumina remain open, reinforcement of the cell wall |
| | | | | Cellulose and its derivatives | | | |
| Bacterial nanocellulose [210] | 55–94 | unaesthetic layer on the surface, wood yellowing or whitening | . . . | ncs | . . . | . . . | cell lumina filled, coated cell walls, non-stable solution |
| Cellulose nanocrystals [210] | 37–84 | ncs | . . . | ncs | . . . | . . . | coated cell walls, cell lumina empty, poor wood penetrability, non-stable solution |
| Nanocellulose whiskers [211] | poor | . . . | . . . | . . . | . . . | . . . | poor wood penetrability, non-stable solution |
| Crosslinkable cellulose ethers [92,212,214] | . . . | . . . | . . . | . . . | . . . | - | high affinity to lignin, limited penetrability |
| 6-deoxy-6-(ω-aminoethyl) amino cellulose, 6-deoxy-6-(ω-hydroxyethyl) amino cellulose [215] | effective stabilisation | . . . | + | . . . | . . . | partly | improved wood penetrability |

**Table 2.** *Cont.*

| Method | ASE [%] | Appearance | Mechanical Properties | Moisture Properties | Resistance to Fungi | Reversibility | Other |
|---|---|---|---|---|---|---|---|
| | | | | Lignin and its derivatives | | | |
| Lignin nanoparticles [210] | 51–88 | depositions on wood surface, darkened wood colour | . . . | ncs | . . . | . . . | non-stable solution, poor penetrability, coated cell walls and filled cell lumina |
| Isoeugenol [217,218] | effective stabilisation | . . . | . . . | . . . | . . . | . . . | in situ polymerisation |
| | | | | Chitosan and guar | | | |
| Chitosan [211, 220,221,225] | effective stabilisation | . . . | + | . . . | + | potential re-conservation | good penetrability, cell lumina remain open |
| Guar [221] | effective stabilisation | . . . | + | . . . | . . . | . . . | good penetrability, |
| Chitosan-based supramolecular system [226] | effective stabilisation | . . . | . . . | . . . | . . . | . . . | Multifunctional system: stability, chelating Fe ions, protecting against biodegradation |
| | | | | Oligoamides | | | |
| polyethylene-L-tartaramide, polyethylene-D(+)-glucaramide, polyethylene-$\alpha,\alpha$-trehaluronamide [227] | 18–35 | . . . | . . . | + | . . . | . . . | high affinity to lignin, good penetrability |
| oligo ethylene-L-tartaramide, oligo esamethylene-L-tartaramide, copolymer between ethylenediamine, adipic and tartaric acids, allyl $\alpha,\alpha'$-trehalose/vinyl alcohol copolymer [228] | effective stabilisation | . . . | . . . | . . . | . . . | + (for oligoamides) | high affinity to lignin, good penetrability |
| | | | | Other natural compounds | | | |
| Colophony and Rosin [58,92,128,202, 229–231] | effective stabilisation | wood darkening possible | . . . | + | + | ? | good penetrability, cell walls encrusted, cell lumina remain open |
| Polyhydroxylated monomer synthesised from $\alpha$-pinene [232] | . . . | . . . | . . . | . . . | . . . | . . . | hydrogen bonding with wood polymers |

**Table 2.** *Cont.*

| Method | ASE [%] | Appearance | Mechanical Properties | Moisture Properties | Resistance to Fungi | Reversibility | Other |
|---|---|---|---|---|---|---|---|
| | | | Halloysite nanotubes (HNT) | | | | |
| HNT/beeswax [236] | 85 | … | … | … | … | … | filled cell lumina |
| HNT/wax Pickering emulsion [237] | 87 | ncs | + | … | … | … | filled cell lumina |
| HNT/Rosin [238,239] | 36–65 | … | … | … | … | … | filled cell lumina |
| HNT/PEG/$Ca(OH)_2$ [240] | … | … | + | … | … | … | filled cell lumina, wood deacidification |
| | | | Organosilicon compounds | | | | |
| Silicon polymer + crosslinker + catalyst [126,202,244,245] | 82–90 | ncs | ncs | … | … | - | good penetrability |
| Selected alkoxysilanes and siloxanes [35,247,248,251] | 81–98 | wood colour can change, depending on the chemical | + (except amino compounds) | … | + | potentially reversible or retreatable, depending on the chemical | good penetrability, smaller molecules bulk the cell wall, bigger fill the cell lumina |
| | | | Other polymers | | | | |
| Phenol-formaldehyde [254] | effective stabilisation | ncs | + | … | … | -, retreatable | cell lumina remain open |
| Melamine formaldehyde (Kauramin) [211,256–259] | excellent dimensional stabilisation | unaesthetic coating on the surface, lighter tone of wood colour | + | + | … | - | time- and cost-efficient method |
| Activators regenerated by electron transfer for atom transfer radical polymerisation (ARGET ATRP) [260,261] | 77–998 | slightly lighter wood colour | … | … | … | retreatable | cell lumina remain open |

There are plenty of interesting ideas for new consolidants, but extensive research is needed on their effectiveness, reliability, durability and safety before they could be proposed as new methods for conservation practice.

## 6. In Situ Preservation and Reburial

The number of known submerged archaeological sites is enormous, and the development of modern non-invasive searching methods (e.g., airborne laser scanning) results in several new significant sites being discovered every year worldwide. In Denmark alone, there are currently at least 18 sacrificial sites located in water meadows and bogs that were used by the local Iron Age population [45], while in Danish territorial waters, around 20,000 shipwrecks and a similar number of various prehistoric settlements are buried [57]. All of them contain countless waterlogged artefacts made of wood, bone, leather, amber, glass and metal; most of them have not yet been excavated. The funds necessary to excavate, document, properly conserve, store or exhibit all the historical objects buried there are inconceivable and simply impossible to obtain. Then, it becomes a question of whether it is necessary to excavate all the discovered archaeological sites? Since numerous findings date back to a similar period, perhaps it is more reasonable to leave them as they are, in situ, for future archaeologists [45,57,262]?

Obligation to preserve archaeological sites and underwater cultural heritage and consider their in situ preservation as the first option was legitimised inter alia by the Valletta Convention For the Protection of the Archaeological Heritage of Europe in 1992 [263] and the UNESCO Convention on the Protection of Underwater Cultural Heritage in 2001 [264]. Where it is not possible or when the excavation of an artefact is justified by exceptional historical, scientific or conservation reasons, the recovery may be authorised, or rescue excavation must be undertaken if the object is anyhow endangered.

The recommended long-term protection of waterlogged artefacts in natural environments employs one of the two available techniques: in situ preservation or reburial. "In situ" means that the object will remain on-site, exactly where it was discovered, while reburial allows for its excavation (and possibly a non-destructive examination) and then reburial (in one piece or in parts) in the same or another environment [262]. Complete understanding of the waterlogged environments with all the biological, physical, chemical and geological processes that happen there as well as wood deterioration processes is fundamental to effective in situ preservation of wooden cultural heritage [9,57,262,265].

Waterlogged archaeological wood can survive in the natural environment only under specific conditions that preclude the growth of wood degraders (more details about wood degradation is given in part 2. Degradation of waterlogged wood). In water ecosystems, such conditions are available in anoxic or dysoxic sediments, where wood can be preserved even for hundreds of years, while the exposure to an oxygenated water column limits the time to only a few years (e.g., three years in the Mediterranean Sea). Therefore, for reburial, usually marine or freshwater sediments are used; sometimes, additional cover materials are applied onto the object or the covering sediment layer, including concrete blocks, sandbags, plastic or geotextile, to prevent its re-exposure to oxygenated water [262,265]. In terrestrial habitats, favourable conditions for wood preservation can be found in bogs, wetlands, or highly saturated soil, particularly if they are permanently saturated [8,9,45,266]. The key factor for effective in situ protection is to restore oxygen-free conditions in the environment. It was shown that even heavily degraded wood, almost completely deprived of polysaccharides, can still serve as a substrate for white-rot fungi under oxygenated conditions, e.g., upon desiccation of submerged areas; another threat related to desiccation is a permanent collapse of degraded wood [25,45].

Regardless of whether it is reburial or in situ preservation, a range of specific environmental parameters must be identified before deciding about the place of wood deposition and then carefully monitored to ensure the continuity of preserving conditions. The most important parameters measured are: dissolved oxygen content—based on this parameter, the sites can be classified as oxic ($>3.0$ mg $L^{-1}$), dysoxic ($0.3-3.0$ mg $L^{-1}$), suboxic ($0.01-0.3$ mg $L^{-1}$), and anoxic ($<0.01$ mg $L^{-1}$); based on the presence or absence of soft-rot fungi, the environments can be classified as aerobic or anaerobic; oxygen levels below 0.3 mL $L^{-1}$ are considered low enough to prevent the growth of any microorganisms, hydrogen-ion concentration (pH)—highly influenced by biodegradation of organic material (can be used as a highlighter of its different phases); extremely high or low pH can accelerate the decomposition of organic matter; most waterlogged environments maintain a neutral or slightly alkaline pH; wood-degrading bacteria generally have a wide range of pH tolerance, redox potential (Eh)—highly influenced by biodegradation of organic matter, anaerobic environments usually have negative redox potentials while aerobic environments have the opposite, the level and duration of saturation—the degree of sediment saturation affects their chemical characteristics and it corresponds to the level of oxygenation; the longer duration of saturation the greater potential for wood preservation, temperature—directly affects microbial activity (low temperatures suppress, and higher temperatures promote it) [8,9,45].

There are also other parameters that can be used to characterise the environment, including the presence of specific reduced or oxidised ion species, salinity or depositional processes. It is important to understand that the mentioned parameters describe different processes that are intertwined and mutually dependent; therefore, they should be considered all together while assessing the preservation potential of a specific site [8,9].

One of the better-researched examples of in situ preservation is the Nydam Mose archaeological site in Denmark [45,267]. Based on the experiences gained from that place, six critical steps to ensure a successful in situ protection have been developed: determination of the area of an archaeological site, identification of the types and the degree of degradation of archaeological materials present, characterisation of the environment on the archaeological site and in the surrounding area, and identification of the most substantial threats to it, development of the best solutions to mitigate deterioration on the site, monitoring of the environment and the state of preservation of artefacts [267].

With proper planning and monitoring, reburial and in situ preservation seem to be an effective way to protect large archaeological sites and artefacts buried there for a long time for reasonable financial investments.

## 7. Discussion and Conclusions

Wooden archaeological artefacts can survive for tens of thousands of years if they are buried in anoxic waterlogged conditions. Under such conditions, bacterial degradation of the holocellulose occurs, but the lignin is largely left intact. The remaining lignified wood structure can give every appearance of being intact, but has very limited mechanical strength and can be easily damaged. The sequence of attack by bacteria and the species involved is not completely understood, although erosion bacteria appear to be the primary degraders. Once degradation begins, a bacterial consortium is formed, which in anoxic conditions will include sulphur reducing bacteria if there is a source of sulphate ions. Where iron is also present, this can result in the deposition of iron sulphides in the wood, which are extremely difficult to remove. This can be a particular problem with large marine artefacts. The bacterial species that are present in the site and their modes of action is poorly understood, as is the influence of site factors, such as pH, redox potential, etc.

Once waterlogged wooden objects are removed from the burial environment they can become susceptible to soft-rot attack and must be stored under appropriate conditions to prevent this from occurring. Soft-rot attack can also occur during burial if the site periodically becomes oxygenated. Once conservation is initiated, it may be necessary to remove contaminating salts by using running water, which can take many years for large objects. If recirculation is used there is a likelihood of microbial contamination occurring and a broad spectrum biocide is normally used to prevent this. As noted, iron sulphides are especially recalcitrant, although other iron salts can be removed using sequestering agents.

We do not have a unified methodology on how to examine degraded wood and the environment from which it is excavated—therefore, we cannot predict/model the degree and pattern of wood degradation (and propose an appropriate conservation method in advance), but every single time we have to measure all the parameters we need. The same relates to the assessment of the effectiveness of the conservation treatment. We measure shrinkage and ASE, but this relates only to the specific wood we are examining, so it is difficult to compare the effectiveness of different types of treatment when it is applied to different woods (different species, degree of degradation, type of degradation, etc.).

Consolidation of waterlogged archaeological wood is undoubtedly a complex and challenging task at the borderline of science and art. It aims to preserve the dimensions and overall appearance of a tangible wooden artefact to make its intangible history and artistic value accessible to the present and future public. Multidisciplinary knowledge is then required to properly maintain wooden artefacts—knowledge about wood as a material, its degree of degradation, degradation processes (including their culprit and the effect on the wood), the impact of different environmental factors, chemistry and physics of consolidants and consolidated wood, sometimes art and historical context, conservation ethics, health and safety issues during both the treatment and then exhibition.

Thus far, we have not found the perfect consolidant which should be effective in providing wood integrity and dimensional stabilisation, compatible with wood, cheap, inert, easily delivered, resistant to ageing and provide a reversible treatment. There are particular problems with alum, which was one of the first consolidants widely used (especially in Scandinavia). This is being manifested as severe degradation of wooden artefacts, some of which have been destroyed. PEG appeared to be close to providing the best prospects as a consolidant, but it is now realised that this also has problems. The participation of PEG in redox reactions with iron during the conservation process is a disturbing finding, with serious implications for the use of PEG as a consolidant [113]. There are many different consolidants that have been tried and research is continuing in this area. Organosilicon compounds appear to show promise, because they can form inert structures within the wood and there is a wide variety of different chemical structures available. However, polymerisation of organosilicon monomers in the wood is likely to result in polymers that cannot then be subsequently removed. Sugar alcohols continue to be used for smaller objects especially, but do not provide sufficient strength to larger degraded objects in order for them to be self-supporting. The Kauramin method (a melamine-formaldehyde mixture) is undoubtedly successful, but irreversible. However, this would appear to be a very attractive option for artefacts that would be destroyed if they were not treated.

Legacy issues, such as treatment with alum, are causing very serious concerns. Retreatment of the Oseberg finds is an extremely challenging task. The aims of such treatment would be to provide mechanical integrity as well as de-acidification of the wood. Tests have been conducted using impregnation with PEG solutions, followed by freeze-drying or Kauramin solution followed by air drying. However, many of the more fragile objects do not survive the aqueous immersion process. For such objects, solvent-based consolidation treatments are being studied [95]. Other possibilities to be explored include supercritical $CO_2$ delivery, or a vapour treatment, combined with in situ polymerisation. If polymerisation within the wood structure is attempted then it must be ensured that the polymerisation process does not result in distortion of the wooden objects.

Regarding the degradation of the Vasa, the crucial questions are: is the degradation reaction an ongoing process or are the oxidative reactions related to the conservation treatment process? Is the degradation linked to a Fenton’s reaction, or simply a result of the reaction between iron sulphides and water? If Fenton’s was the main reaction responsible for degradation, then it would be expected that oxidation of the lignin content would be occurring, which does not appear to be the case. There are serious challenges involved in removing the already created sulphuric acid from such a large structure, or with ensuring that any treatment involving neutralisation is able to fully penetrate to all the regions where the sulphuric acid is present. Similar issues are being encountered with the Mary Rose and other large marine structures where both iron and sulphur are present. An alternative approach would be to provide an envelope in the wood surface region that prevents oxygen ingress and hence limits oxidation reactions, although this does not deal with the presence of sulphuric acid which is causing damage to the polysaccharide components in the wood.

In the future, will the excavation and display of large timber structures be considered effective, or will new methods of display be used, such as laser scanning combined with virtual reality, or display in situ within immersion chambers? For most sites, once excavation has revealed the necessary information and context, reburial is the only option, with only the smaller objects being subjected to conservation. Sites, such as Must Farm and Flag Fen in Cambridgeshire UK, will be protected by ensuring that the water levels on the sites do not drop to a point where oxygenated conditions are encountered [268].

“Blessed were the ancients, for they had not antiquities”—Italian saying [269].

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