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Conservation and in situ preservation of wooden shipwrecks from marine environments

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ABSTRACT

Wooden shipwrecks in the marine environment form a large part of the underwater cultural heritage. Over the past 50 years several wrecks have been excavated, raised and conserved. In the recent past there has been a trend towards preserving these sites in situ, on the seabed, as opposed to raising them. This article gives a brief overview of the deterioration of wood in the marine environment and the principles of the most commonly used methods for conserving waterlogged archaeological wood. Furthermore, a general approach to tackling the in situ preservation of wooden wrecks sites is given.

1. Research aims

To ensure the survival of the greatest possible number of finds, it is necessary, through research, to develop new methods, which are not only technically superior to the existing ones, but also quicker and more cost effective. This is in order to maximize the benefit of our limited resources and secure our cultural heritage for generations to come. For in situ preservation this includes improved assessment of sites and finds; methods to mitigate deterioration, and monitoring techniques. For conservation the main areas to develop and improve are methods for assessing the state of preservation of wood in situ, impregnation agents and drying methods.

2. Introduction

When a wooden shipwreck is discovered in the sea and it is judged to be of significant archaeological or historical importance archaeologists and conservators are faced with two courses of action: excavating, raising and conserving the find or preserving it on the seabed in situ (Fig. 1). If the wreck is to be raised, with the intention of conservation and exhibition, it is advisable at the excavation stage to know what the end use of the artifact will be, along with the state of preservation of the wood. These parameters will determine the physical raising of the timbers, choice of conservation method and have implications for the curation of the conserved find. However, if it is desirable to preserve the wreck site in situ on the seabed, it is again necessary to know the state of preservation of the timbers and the natural processes of deterioration. In this way we can see which processes can affect the wood in the future, how these can be mitigated for, if necessary, and the site subsequently monitored to ensure its safeguarding.

This article focuses upon the main approaches conservators and archaeologists around the world have taken to addressing these two options.

3. Deterioration of wood in the marine environment

Waterlogged archaeological wood differs from recent wood as it has been affected by a range of deteriorative agents operating in underwater environments. Fig. 2 shows an idealised view of a wooden shipwreck as it may appear after the wrecking process. Effectively parts of a wreck can be exposed to two very differing environments – the open seawater and the sediments of the seabed.

In the open seawater sediment erosion, or scour, in conjunction with wood boring organisms (shipworms and gribble), can lead to the relatively rapid deterioration of those upper parts of a wreck which are not covered by sediment.

However, if the wreck is covered by sediment, the wood will not be degraded by wood borers due to limited dissolved oxygen in the water, which prevents their respiration [1].

Instead, deterioration in waterlogged anoxic sediments is primarily caused by “erosion” bacteria. Fortunately these bacteria primarily degrade the cellulose and lignin within the innermost

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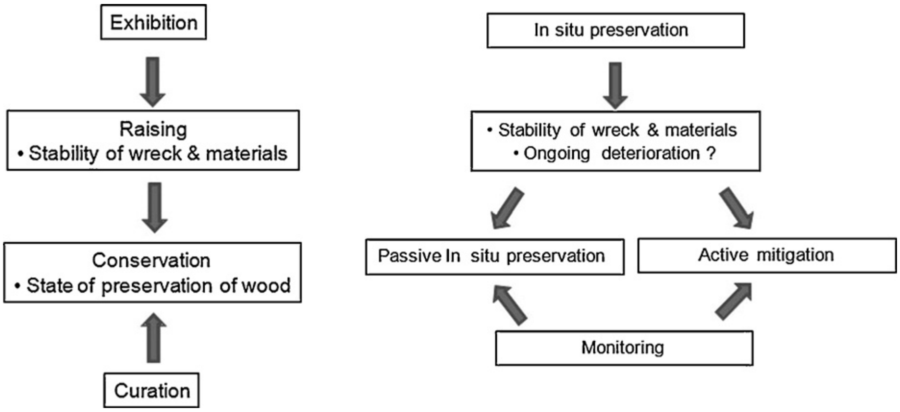

Fig. 1. Actions and requirements for in situ preservation and/or conservation of waterlogged archaeological wood from marine archaeological sites.

part of the wood cell wall and although they may modify the lignin in the compound middle lamella, they do not completely degrade it. Hence, the lignin rich compound middle lamella survives and its form is kept intact by the degraded parts of the cell being replaced by water. Thus if waterlogged wood from shipwreck sites has been buried in sediments it is often in a very good state of preservation, archaeologically speaking, as all surface details, such as carvings or tool marks, are preserved. Nevertheless, archaeologists, conservators and museum curators require that the raised objects are in a dry and stable condition making them readily available for scientific analysis, exhibition or storage. Unfortunately, if wooden finds are not dried under controlled conditions, they will be damaged and hence the need for conservation.

4. The conservation process

4.1. From a wet unstable to a dry stable condition

Uncontrolled drying can lead to: collapse, shrinkage, distorted shape and surfaces (twists, cracks, splits), disintegration, precipitation of salts and corrosion products in the wood, as will be discussed. All types of damage are the result of uncontrolled removal of the free/capillary water in the cell lumen and the hygroscopically bound water in the cell wall.

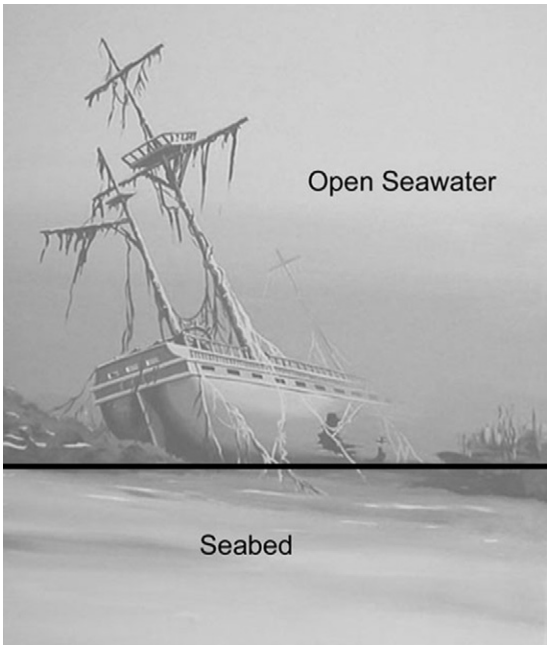

Fig. 2. An idealised shipwreck on the seabed showing how parts can be exposed to open seawater and/or buried in the seabed. These two different environments will affect the deterioration processes acting upon the wood.

4.1.1. Collapse

Collapse develops during drying of the free water, if the contractile forces, caused by capillary forces of the water meniscus, exceed the compression strength of the object. Collapse is irreversible and recognized as flattened cells (in cross section), a very dense structure and "wavy" surface (in the radial plane). This can be reduced, or prevented, by minimising the surface tension of the water during the drying/dehydration process, or by fixation of the wooden object in the water-swollen stage.

4.1.2. Shrinkage

Shrinkage is caused by removal of the hygroscopically bound water, sorbed in the cell wall. The loss of bound water results in a volumetric reduction of the cell wall and is recognized as cracks–both in the longitudinal and transversal direction of the wood. This can be avoided or reduced by replacement of the bound water with a bulking agent or by fixation of the cell wall in the water-swollen stage.

4.1.3. Other causes of damage

Disintegration and warping are caused by both collapse and shrinkage. Problems with salts and corrosion products will be discussed in other articles within this volume.

4.2. Selection of the optimal conservation process

An acceptable conservation result is best achieved through a close cooperation between the archaeologist, the conservator and the end-user (museum, curator). The conservation process is therefore a combination of: assessment of the find, best available technical conservation methods, demands to the end-use and the resources available. Furthermore, methods also have to take aesthetic, ethic, health and environmental aspects into consideration.

4.2.1. Assessment of wooden objects

Density is a good parameter to assess the overall state of preservation of waterlogged archaeological wood [2]. As discussed, bacteria remove cell wall material, thus the more degraded the wood is, the lower the density. Erosion bacteria primarily remove cellulose and can reduce the density of wood to below 150 kg/m^3, approximately the density of the compound middle lamella. However, even at densities of 400 kg/m^3 (fresh oak wood is approximately 600 kg/m^3) there is a need for conservation in order to prevent shrinkage and collapse [3].

Density can be assessed using cores taken in situ with an increment borer or by non-destructive methods such as a Pilodyn wood tester [4].

4.3. *Technical conservation methods*

The most frequently used conservation methods to prevent shrinkage and collapse in waterlogged archaeological wood are:

- full impregnation with water-soluble agents, such as polyethylene glycol (PEG), sugar (sucrose, mannitol, sorbitol, lactitol). These agents fill the cell lumen, replace the free water through osmotic exchange, and solidify at room temperature fixing the cell structure in the water-swollen stage;
- controlled air drying after partial impregnation with water-soluble agents (PEG, sugars). The removal of excess water by controlled air drying causes the agents to solidify;
- freeze-drying (vacuum and non-vacuum) after partial impregnation with water-soluble agents (PEG, sugars);
- partial impregnation with agents (Kauramin, polyester resin), which partially fill and replace the free water in the cell lumen and polymerise and solidify upon curing;
- exchange of the free and bound water with organic solvents with a low surface tension (cellosolve-petroleum, ethanol-ether, acetone, super critical carbon dioxide) followed by drying and impregnation (curing and non-curing agents).

4.3.1. *Full impregnation with water-soluble agents*

The free and bound water in the wood cell are replaced with a water-soluble impregnation agent, through a process of diffusion at elevated temperatures. The cells are fixed in the wet/swollen state, thus preventing collapse and shrinkage when the impregnation agent solidifies at room temperature. Impregnation agents with molecular masses higher than 6–800 g/mol can only penetrate the cell lumen and act as a void filling agent after solidification and are primarily used to prevent collapse. Molecules with molecular masses less than 600 g/mol, for example: alum, sugars (sucrose, mannitol, sorbitol, lactitol) and low molecular mass PEGs (200 to 600 g/mol) are able to enter the cell wall and replace the hygroscopically bound water and are primarily used to reduce shrinkage of the wood.

Impregnation normally requires immersion of the objects, as spraying, painting or coating with agents is often insufficient. Tanks for impregnation must be resistant to any corrosive effects of the agents and be strong enough to support the weight of the water and timbers. Microbial activity will be prevalent with most impregnation agents, whether or not biocides should be added is dependent upon local legislation, disposal possibilities and the practical set up of the conservation laboratory.

4.3.1.1. Full impregnation with polyethylene glycol (PEG). PEG, with the general formula $H_2OCH\,(CH_2OH_2)\,CH_2OH$, is a synthetic material with a range of molecular masses. The low molecular mass PEGs (200 to 600 g/mol) are liquid at room temperature, the intermediate PEGs (800 to 1000 g/mol) are paste like and the high molecular mass PEGs (1500 to 10,000 g/mol) are solid at room temperature. All PEGs are soluble in water and several alcohols and their hygroscopicity and solubility in water increases with decreasing molecular mass (Fig. 3). Impregnation can take place as a 1- or 2-step process.

4.3.1.1.1. 1-step process. After immersion in water the concentration of high molecular mass PEG (1500 to 4000 g/mol) is increased stepwise, starting at 10% ending as close to 100% as possible. The impregnation from 10 to 50% can be carried out at room temperature, above 50% the solution must be heated in order to remain liquid. Heating should be carried out with caution and not exceed 60 °C, so as to prevent degradation of the PEG and wood. Alternatively, the PEG concentration can be increased by allowing water to evaporate from the solution. The maximum concentration that can be achieved is between 85 and 95% due to the PEG taking up moisture from the air. When objects are taken out of the tank and while the impregnation agent is still liquid, hot water or steam can be used to remove surplus PEG, and the wood can be left to cool and the agent solidify.

4.3.1.1.2. 2-step process. This process uses both low- and high-molecular mass PEGs. In the first step, the wood is impregnated with low molecular mass PEG (200 to 600 g/mol), which serve to bulk the cell wall. The concentration increasing stepwise to between 10 and 40% [5]. At this stage, the impregnation solution is replaced with a new solution of high molecular mass PEG (2000 to 4000 g/mol), which serves to stabilise the cell structure. The initial concentration of the second solution is 10 to 20% higher than the final concentration of the first solution. The concentration of high molecular mass PEG is then increased stepwise following the same principles as for the 1-step method.

4.3.1.1.3. Advantages. Full impregnation using high molecular mass PEGs (1-Step process) can be used on wood in all states of preservation but is most applicable to degraded wood without a well-preserved inner zone. It is a robust, reversible, non-toxic, relatively inexpensive method and the wood surfaces can be easily glued after treatment. The wood can be shaped/bent into the right position while the impregnation agent is still liquid. Microbial activity will be lower in solutions with high concentrations of PEG.

Full impregnation by the 2-step method is best applied when the wood is degraded in the outer regions but well-preserved in the centre, as the penetration of low molecular mass PEGs into the cell wall of the well-preserved central part will reduce the shrinkage of these parts of the wood.

4.3.1.1.4. Disadvantages. Both the 1- and 2-step methods produce heavy archaeological wooden objects that tend to have a dark and greasy appearance if the surfaces are not subsequently treated. PEG is corrosive and cannot be recommended for impregnation of objects containing preservation worthy metal parts. When the concentration exceeds 50% and circulation and heating of the baths is applied, the process must be closely monitored as if heated too quickly, osmotic collapse of the wood may occur along with degradation of the PEG. There are some particular concerns regarding the 2-step method, as the low molecular weight PEG remains liquid at room temperature. If there is an excess of the agent present in the wood, the PEG will slowly drift “downwards” into the wood due to gravity, concentrating in the lower parts of the object and give a wet and sticky surface. Moreover, the low molecular PEGs are very hygroscopic and treated objects are vulnerable to the effects of high relative humidity in the museum environment. Furthermore, if inorganic elements are present in the wood, the bound water in the low molecular mass PEGs may lead to an increased ionic mobility [6].

4.3.1.2. Full impregnation with sucrose and lactitol. Most commonly sucrose and to some extent lactitol are used for full impregnation of waterlogged wood. Sucrose, also known as table sugar, is a disaccharide and has the structural formula $C_{12}H_{22}O_{11}$ its molecular mass is 342. Lactitol (4-O-β-D-galactopyranosyl-D-glucitol) monohydrate is a sugar alcohol with the structural formula $C_{12}H_{24}O_{11}$ and molecular mass 344. Both sugars are solid at room temperature and are readily soluble in water. The impregnation processes for both sugars are similar, whereas the drying stages differ. Objects are immersed in water and sugar is added to increase the concentration stepwise. Owing to the low molecular mass of the sugars, the initial concentration can be 20 to 25%. Impregnation can take place at room temperature, which is more time consuming but more energy efficient, or at elevated temperatures up to 60 °C. At room temperature, the final concentration will never exceed 64–67% due

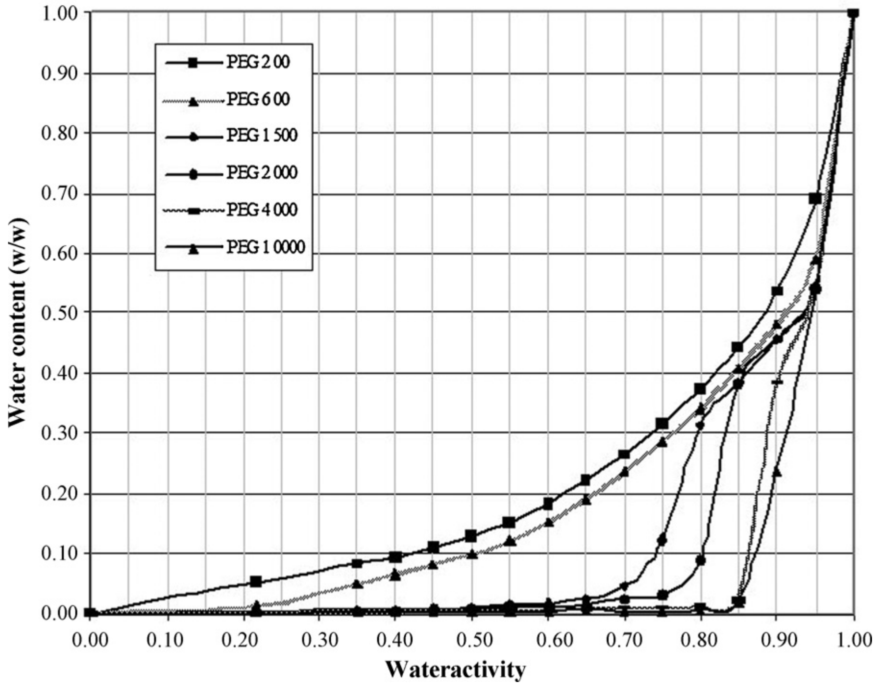

Fig. 3. Moisture sorption isotherm for polyethylene glycol (PEGs) with molecular masses between 200 and 10,000 g/mol.

to solubility constraints of the sugars. If the solution is heated to 50 °C, concentrations of 75% can be achieved; this increases the impregnation rate and reduces the risk of microbial attack.

Upon cooling, sucrose will precipitate and crystallise in the cell lumen and to some extent the cell wall, reducing both collapse and shrinkage. While the solution is still liquid, hot water or steam can be applied to remove excess sucrose from the surface. The water remaining in the wood at room temperature is removed by evaporation when the relative humidity around the object is reduced stepwise.

When lactitol impregnated wood is taken out of the hot impregnation tank, the crystallisation process is initiated by spreading lactitol crystals on the wet surface. The best drying results are achieved if performed at 50 °C. Lactitol can form four types of crystals upon drying (lactitol anhydrite, -monohydrate, -dihydrate and–trihydrate). Formation of trihydrate crystals causes a large volumetric expansion, which will destroy the surface of degraded wood. The risk is reduced if drying takes place at high temperatures (50 °C) or by adding 10% Trehaloses (α-D-glucopyranosyl-α-Dglycopyranoside) to the impregnation bath [7].

4.3.1.2.1. Advantages. The low molecular masses of these sugars gives good penetration into the wood enabling the conservation of relatively well-preserved large objects, which do not have a tendency to collapse. The impregnation agents are not corrosive, sucrose is easily available and disposal after conservation is unproblematic. As the wood is still wet when taken out of the impregnation tank, there is time to work with the final shaping of the timber before drying. Both sucrose and lactitol can, if necessary, be removed from the wood by immersion in water at a later stage.

4.3.1.2.2. Disadvantages. The biggest disadvantage using sugars is the risk of microbial or insect attack during impregnation and after conservation, if not carried out or subsequently stored in controlled conditions. Although biocides can be added to the solution, microbial growth is extremely difficult to control. Microorganisms and insects can cause degradation of the sugar; sucrose can be converted to fructose and glucose leaving a sticky and foul smelling solution that is unable to crystallise upon drying. If this occurs, a total replacement of the bath and thorough cleaning of the wood may be necessary [8,9].

4.3.2. Controlled air drying after partial impregnation with water-soluble agents

Controlled air drying can be applied to objects partially impregnated with water-soluble agents. Large objects can be encapsulated in climate tents, small artefacts in polyethylene bags/boxes. The success of the method will depend upon the degree of degradation of the wood, the effectiveness of the impregnation pretreatment and the rate of reduction in relative humidity in the air surrounding the objects. The wood is dried by stepwise reduction of the relative humidity of the surrounding air. To ensure that high moisture gradients are avoided, as these will cause cracking, monitoring at the wood surface and centre of the wood should be carried out. The moisture content of the wood in the centre has to be between 80 and 90% of the surface value before proceeding to the next step of reducing the relative humidity. Drying agents such as dry paper tissue, dry pieces of wood, silica gel or molecular sieves can be applied to reduce the RH of the air surrounding the objects. Alternately, electric dehumidifiers can be used.

4.3.2.1. Advantages. The method is relatively cheap as regards equipment required.

4.3.2.2. Disadvantages. The end result of conservation by this method is very variable, for example if the wood is too degraded, impregnation insufficient, or the drying rate too fast, severe cracks and shrinkage can occur.

4.3.3. Freeze-drying

The principle of using freeze-drying for conservation of waterlogged archaeological wood is to reduce capillary forces, which normally develop when water evaporates from the water meniscus in the small pores in the wood. These forces are avoided by freezing the water to ice and drying through sublimation, thus avoiding the liquid phase of water. The sublimation, and thereby the freeze-drying, starts when the partial pressure of water vapour in the air

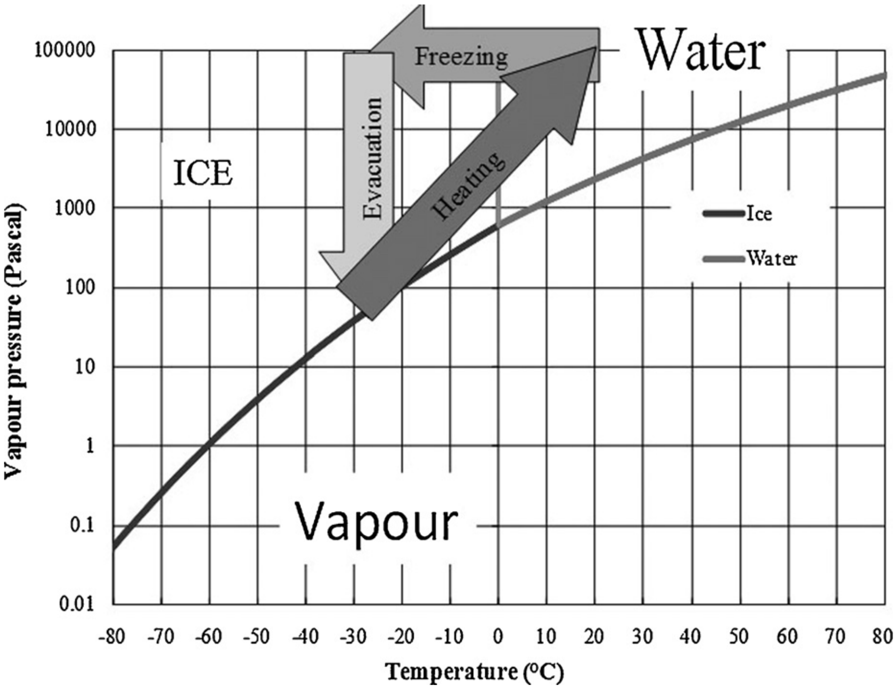

Fig. 4. Water Vapour pressure over water and ice and the three stages of the freeze-drying process. Freezing > evacuation/sublimation > Heating of object as a result of pressure and temperature equilibration to ambient laboratory conditions, followed by heating and plus principles for freeze-drying in relation to the liquid, solid and gas phase.

around the object is lowered below the partial pressure of saturated water vapour over the ice (Fig. 4). Freeze-drying from pure water can take place at temperatures below 0 °C and partial water vapour pressures below 610 Pa.

Although freezing to a certain extent fixes the cell wall in the water-swollen state, drying is normally not done from pure water, as it will result in expansion and cracks in the object when the free water in the cell lumen freezes. Additionally shrinkage, disintegration and cracks occur when the hygroscopically bound water in the expanded waterlogged cell wall is removed.

These problems can be avoided by 35–45% pre-impregnation of the waterlogged object with water-soluble impregnation agents as described in Section 4.3.3.1. The introduction of impregnation agents lowers the freezing point of the solution and, as the freeze-drying process requires a total solidification of the solution, the process temperature must normally be kept below the eutectic/collapse temperature of the solution. Fig. 5 shows the eutectic temperature of PEG as a function of the molecular mass. Normally PEGs with molecular masses above 1500 are selected, as smaller PEGs are not solid at room temperature and their eutectic temperatures are very low, making freeze-drying difficult.

The sublimation of ice takes place from a retreating ice front in the wood and the speed of the freeze-drying process is nearly proportional to the water vapour pressure over ice at the freeze-drying temperature [10] Therefore, the freeze-drying process is a compromise of many parameters, for example lowering the temperature in the object to the eutectic temperature of the PEG also lowers the water vapour pressure and subsequently slows down the process.

The freeze-drying process consists of two phases, following impregnation with water-soluble impregnation agents. First, the object is frozen and thereafter freeze-dried either under vacuum or at atmospheric pressure.

4.3.3.1. Vacuum freeze-drying. Vacuum freeze-drying is commonly used methods for conserving waterlogged archaeological wood. The objects are normally impregnated with stabilizing and bulking agents for example high and low molecular mass PEG up to a maximum concentration of 45%.

Vacuum freeze-driers for processing waterlogged archaeological objects, pre-impregnated with PEG, consist typically of a vacuum chamber, with walls that can be cooled, a connection between the vacuum chamber and the ice condenser fitted with a valve and an ice condenser connected to a vacuum pump (Fig. 6). The chamber must be able to reach temperatures below the eutectic temperatures of the aqueous PEG solution and a pressure where the ice in the object can sublimate. The temperature in the ice condenser must be low enough to condense the water vapour sublimed from the object in order not to overload the vacuum pump. Depending upon the thickness of the object, drying can take anywhere between one and six months.

4.3.3.1.1. Advantages. Vacuum freeze-drying is probably the most reliable conservation method with very few health, safety and environmental problems. The treated objects are light in weight and colour and the objects can be dried over moulds to obtain the correct shape so only minimal processing is needed during mounting for display.

4.3.3.1.2. Disadvantages. The equipment is expensive, relatively complicated with high running costs. If objects have not been shaped prior to freeze-drying they must be heated and humidified in order to shape them. The PEG used for impregnation does not always add any strength to the object, so a suitable support may be required. Objects thicker than 10 cm are difficult to vacuum freeze-dry.

4.3.3.2. Freeze-drying at atmospheric pressure. The use of freeze-drying at atmospheric pressure has only been reported in a few cases [11], and the method has not been developed to a level where it can be considered a standard method. However, it might be an inexpensive alternative to vacuum freeze-drying for both small and large objects. Standard freezing containers or rooms with different types of dehumidifiers for use with large objects are currently under investigation and processes for use in connection

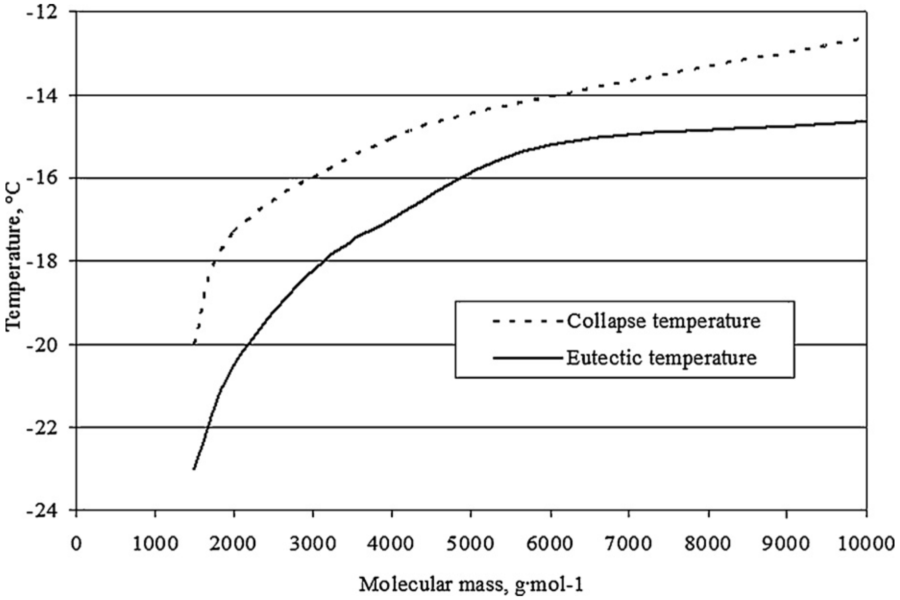

Fig. 5. Eutectic and collapse temperatures for aqueous polyethylene glycol (PEG) solutions, as a function of the molecular mass.

with household freezers and freezing-cabinets for smaller objects are being developed.

4.3.3.2.1. *Advantages.* The method is simple with the equipment being readily available and relatively inexpensive. The drying time for objects up to a thickness of 1.5 cm is quite fast.

4.3.3.2.2. *Disadvantages.* The method is not well documented. The drying time can be long for objects with thickness of more than 2 cm and therefore resource demanding.

4.3.4. *Impregnation with solidifying and polymerising agents*

The principle is that free water in the cell lumen can be replaced by an impregnation agent that solidifies in the wood upon curing.

4.3.4.1. *The Kauramin method.* Impregnation is carried out with a water-soluble low molecular mass (400 to 700g /mol) melanin-formaldehyde polymer, Kauramin CE. The initial concentration of the Kauramin solution is 25% and good dimensional stability can be obtained after impregnation to 35–45% [12]. Impregnation takes place at room temperature and the pH should be kept at 8 to 9 by adding triethanolamine (TEA). The solution will eventually become acidic, despite adding TEA and when the pH drops to 6–7, the chemicals poly-condensate and form a three-dimensional, insoluble and hard polymer in the wood. Impurities in the bath, oxygen, carbon dioxide, acidity and temperature have impacts on the impregnation and curing process. The impregnation time can take from a few weeks to one year depending upon the size (thickness) and state of preservation of the wood. After impregnation, the wood requires cleaning of surplus impregnation agent from the surface, before the controlled poly-condensation of the agent and controlled drying. The poly-condensation of melanin-formaldehyde lasts 7 to 14 days, depending on dimensions of the objects and takes place at 50 °C with the objects wrapped in wet tissue and plastic foil to avoid water evaporating from the wood before the curing process and stabilisation has taken place. The drying can take place applying vacuum freeze-drying at −5 °C and 400 Pa, in a microwave oven at 35 °C or by controlled slow evaporation.

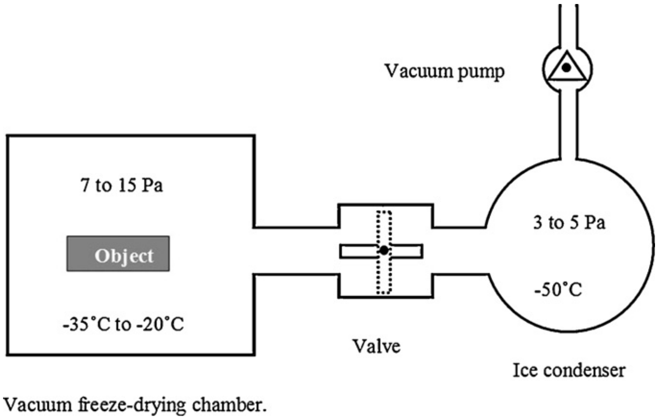

Fig. 6. Principle for vacuum freeze-dryer for drying waterlogged objects pre-impregnated with polyethylene glycol (PEG).

4.3.4.2. *The polyester resin-radiation method.* The polyester resin-radiation method, developed by ARC-Nucléart in Genoble [13] is based upon the principle of dehydrating the waterlogged objects with an organic solvent, often acetone. After dehydration, the object is impregnated with increasing concentrations of acetone soluble polyester resin, (standard Norsodyne® resin, tetrahydrophtalic grade). The Polyester resin solidifies when irradiated with gamma rays, which causes the resin to cross-link and harden in the wood.

4.3.4.2.1. *Advantages.* The Kauramin method produces, after a relatively short treatment time, objects that are light in weight, with dimensions and surface details preserved. Kauramin conserved wood is easily glued and surface treated if necessary. Wooden objects containing inorganic salts such as sulphur or iron become stable when treated with this method. The impregnation solution and the treated objects do not support growth of microorganisms.

4.3.4.2.2. *Disadvantages.* In order to avoid uncontrolled curing during the Kauramin impregnation, the method requires specialised equipment and strict control. The acetone used in the process, along with the gamma radiation are hazardous to health. Furthermore, formaldehyde will occur during heating of the material, thus special laboratory precautions and security are required. Treatments with poly-condensed melanin resin or with cross-linked polyester resin are irreversible.

4.3.5. Exchange of the water by liquids with low surface tension followed by impregnation and drying

4.3.5.1. General methods for dehydration with organic solvents. The principles of all conservation methods using dehydration in organic solvents is that the water in the object is replaced by organic solvents, which have low surface tension and polarity, e.g. ethanol, isopropanol, 2-ethoxy-ethanol and acetone. Replacement of the water with these water-soluble organic solvents reduces contractile capillary forces and thereby collapse during their evaporation. The replacement of water takes place by immersion of the object in successive baths of an organic solvent. If necessary, the object is further immersed in successive baths of solvents with even lower polarity and surface tension e.g.: ether, petroleum, benzene etc.

When all water and intermediate organic solvent are replaced, the object is dried at atmospheric pressure or in vacuum. Stabilizing impregnation agent can be added to the last bath of organic solvent. The agents can be non-polymerising such as waxes, rosin and acryl or polymer forming agents like polyesters and silicon-oils [14].

4.3.5.1.1. Advantages. The advantage of using dehydration with organic solvents is the simplicity and rapidity of the methods. The methods are excellent for composites of wood and metal as non-corrosive impregnation agents can be used. As most of the impregnation agents are not sensitive to high relative humidity or high temperatures, the conservation method makes them less vulnerable to poor climate control.

4.3.5.1.2. Disadvantages. Use of organic solvents can cause health and safety problems and as large amounts of organic solvents are difficult to handle, the method can only be recommended for smaller objects.

4.3.5.2. Super critical drying. Supercritical drying in its present form [15], where the objects prior to drying from supercritical carbon dioxide (31.1 °C and 7.39 MPa) are dehydrated in ethanol, is very similar to dehydration in organic solvents as described above. The exception is that the last bath of organic solvent is replaced with supercritical carbon dioxide, not possessing any surface tension, therefore reducing any collapse so a minimum when off-gassing. The method is complex and expensive and therefore not advantageous compared to dehydration in organic solvents.

4.3.6. Exhibition and storage requirements for conserved objects

All the conservation methods and impregnation agents mentioned are safe to use as long the requirements for normal museum/storage conditions, in relation to temperature (15 to 25 °C), relative humidity (30 to 60%), physical, chemical and biological threats are met.

Apart from objects treated with polymerising agents, all other objects, especially those treated with sucrose, can be damaged by attacks by insect, rodents etc. Therefore, proper pest control is of paramount importance if objects are to survive for longer periods in museums.

The level and fluctuation of relative humidity of the air are of vital importance for wooden objects treated with water-soluble, polar impregnation agents, as both the wood itself and the agents sorb an increasing amount of hygroscopic water with increasing RH. A high level of sorbed water can result in migration of salts and low molecular substances, softening of the objects, which can lead to chemical processes that normally only take place in aqueous solutions. Except for low molecular PEGs and glycerol, most impregnation agents are safe to use up to 60% RH [6]. Furthermore, a high RH can result in fungal attacks. Low relative humidities can result in cracks and shrinkage of objects if hygroscopically bound water is removed from the cell wall. In relation to temperature, mainly high temperatures can cause problems, as the strength of the object can be reduced by softening or melting of the impregnation agents.

As impregnation agents, apart from those that polymerise, do not always add strength to conserved objects, support is often necessary both for exhibitions and storage.

5. In situ preservation of archaeological wood in the marine environment

Although conservation of waterlogged wood has a long history, dating back to the late 1880s, with the use of linseed oil / creosote, alum and other substances to conserve finds such as the Nydam boat and Hjortspring boat in Denmark, and the Oseberg ship in Norway. All these finds were found buried on land in waterlogged conditions. With the advent of the aqualung in the 1940s came the development of underwater archaeology and in the proceeding 40–50 years several underwater sites have been excavated, raised and conserved and exhibited in north west Europe. Notably the Viking Age ships from Skuldelev in Denmark, The *Mary Rose* (UK), The Bremen Cog, (Germany) and *Vasa* (Sweden). These sites have captured the public's imagination about underwater archaeology and provided them with the opportunity to see and learn about the maritime history of Europe. Furthermore it was these finds that contributed to many of the conservation methods discussed in the preceding sections.

Nevertheless, these examples and others from around the world, form only a small fraction of known underwater archaeological sites – in Danish territorial waters alone it is estimated that there are in the region of 20,000 historical shipwrecks (and 20,000 submerged settlement sites where wood form a large part of the finds). As a result of the huge number of sites known and still being discovered due to offshore and subsea development, the past twenty years has seen a move toward in situ preservation, that is to say to protect, monitor and manage underwater archaeological sites where they lie on the seabed. This tendency has been politically galvanised in the 2001 UNESCO Convention for the Protection of the Underwater Cultural Heritage [16], which in essence states that, as a first option, the underwater cultural heritage should be protected in situ and where possible non-intrusive methods to document and study these sites in situ should be used.

In situ preservation is another tool that can be used to safeguard waterlogged archaeological wood. It should not be seen as a replacement for conservation as it is not a panacea and not always the optimal solution for preserving waterlogged archaeological wood. In situ preservation is a nascent discipline, being practiced over the past 30–40 years. Currently there are no standard methods describing step by step how to preserve a site in situ. Nevertheless, for in situ preservation to be feasible and effective, a process based approach to understanding both the wreck site environment and the processes of deterioration is paramount and should include the following five points:

1. the extent of the site to be preserved;
2. the most significant physical, chemical and biological threats to the site;
3. the types of materials present on the site and their state of preservation;
4. strategies to mitigate deterioration and stabilise the site from natural impacts;
5. subsequent monitoring of a site and implemented mitigation strategies.

This article is focused on the preservation of wood, rather than all archaeological materials and points 2 and 3 have been previously

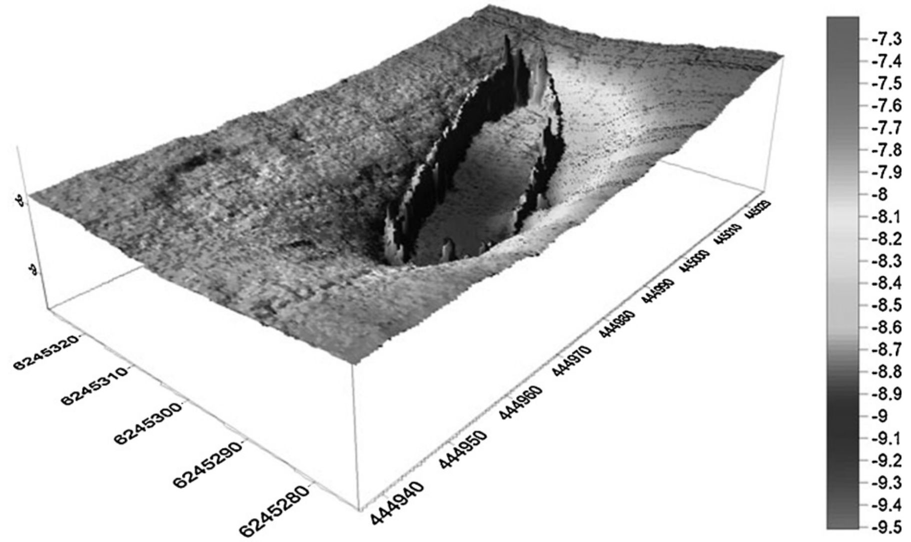

Fig. 7. 3D plot of multibeam sonar survey of the wreck on the *HMS George* wrecked off the west coast of Jutland, Denmark.

discussed, thus the remainder of this section will focus upon points 1, 4 and 5.

5.1. Extent of the site to be preserved

A shipwreck constitutes those parts and materials that have survived the wrecking process and, following a period of deterioration/stabilisation, reached a dynamic equilibrium with its new environment. Archaeological investigations tend to focus on examining the structure of the remaining hull and associated finds. However, low underwater visibility and the overall size of a site can often make it difficult to rapidly get a complete "overview". This is even more apparent when it comes to those parts of the wreck that lie buried within sediments. However, using marine geophysics it is now possible to more rapidly assess the spatial distribution of material both on and within the seabed. Fig. 7 shows a plot of a wreck measured using multi beam sonar, where the remains of the wreck can be seen to sit in a hollow that was caused by scour. Summarily, scour occurs at the seafloor when sediment is eroded from an area in response to forcing by waves and currents and is often initiated by the introduction of an object (e.g. shipwreck) to the seafloor [17]. As a result scour hollows or pits can be formed and in the right conditions can serve as a sink for archaeological material removed from the ship during its deterioration. Quite often the amount of buried archaeology far exceeds what is actually visible on the seabed.

5.2. Strategies to mitigate deterioration and stabilise the site from natural impacts

If an initial assessment of a site's environment reveals that there are natural threats, or the site is unstable, strategies should be implemented to mitigate for these threats. It is at this stage that an overall evaluation of whether it is feasible and responsible to leave the site in situ should be made. In terms of wooden wreck sites, the two most significant threats are the possibility of further physical deterioration, due to scour, and biological deterioration caused by wood boring organisms. Furthermore, there will always be a very slow degradation of wood due to bacterial decay.

To mitigate for these processes, sites are often physically covered using different methods. In the right circumstances, this can both alleviate scour and prevent the activity of wood boring organisms. In other cases, where the local environment is not conducive to simply covering, a site can be excavated and re-deposited/reburied in a more benign environment underwater or on land.

Sandbags are often used as a means of covering and stabilising archaeological sites underwater [18]. However, their deployment is labour intensive, especially when working in areas with strong currents. Recently, attempts have been made to stabilise sites in situ by entrapping sediment particles carried in the water column and creating an artificial seabed, or burial mound, over the threatened site. Notable examples of this are the use of artificial sea grasses on the wrecks of the *William Salthouse* [19] the *James Matthews* [20] and the Hårbølle wreck [18]. Similarly, various types of netting (shade cloth, debris netting, wind netting) have been used on several wrecks in the Netherlands and Sri Lanka [21] and also trialled on the *James Matthews* [20] and the Hårbølle wreck [18].

The artificial sea grass and the various types of net effectively function in the same way. The plastic fronds of the artificial sea grass trap sediment particles in the water column as water passes through them. Due to friction, the water is slowed causing the sediment particles to fall out of the water column resulting in an artificial seabed/mound. In the case of netting, the net is fixed loosely over the structure to be protected, so that it "wafts" in the water column. As with the artificial sea grass, suspended sediment in the water column passes through the net but as it does it is slowed by friction: the sand falls out of suspension and creates a mound under the net. These materials only function in the right conditions: the presence of sediment transport and the particle size of sediments being transported must be assessed prior to applying these methods on sites.

Should the immediate site environment not be conducive to in situ stabilisation of the site, or if, due to subsea development, a site has to be excavated, excavation and reburial in a more benign environment is a further option. Reburial as a means of long-term storage is not a new idea and has been proposed and practised for many years around the world [22]. One of the first attempts of controlled reburial of archaeological remains underwater was carried out in the 1980s. From 1980 to 1984, Parks Canada excavated the remains of the Basque whaler *San Juan* in Red Bay, Labrador. Following the excavation, raising and documentation of the wreck, the timbers were reburied to protect them against biological, chemical and especially physical deterioration due to ice floes [23] What sets this early project apart from other reburial attempts of the time was that monitoring of the reburied timbers and the surrounding reburial environment was planned from the outset. Sandbags and the ballast from the ship were used to construct an underwater cofferdam where the timbers were placed in several layers, each separated by a layer of sand. Modern wood blocks were placed alongside each layer for subsequent removal and analysis and a series of sealed dipwells installed to enable pore water samples from the mound to be removed for analysis. The burial mound was then covered with a heavy-duty plastic tarpaulin anchored by concrete filled rubber tyres.

A similar project building on this work was the reburial of artefacts from the wreck (10,000 were recovered) of the *Fredericus* (1719) in the Swedish island port of Marstrand. Full conservation treatment of all excavated artefacts was considered both impractical and unnecessary from an archaeological perspective and it was decided that 85–90% of the finds should be reburied after proper archaeological documentation [24]. Trenches were dug for the various material types found and covered with at least 50 cm of clay/sand sediment in 2002. The depth of burial was based on previous experiments, which sought to identify the optimal burial depth for materials [25].

5.3. Monitoring of a site and implemented mitigation strategies

In situ preservation should not stop once the site has been stabilised. Monitoring of stabilised sites is necessary to ensure continued stability. Furthermore, although a newly discovered site may be relatively stable and thus not immediately require any active mitigation strategies, environmental and/or physical changes may occur which necessitate mitigation strategies at a later date. In this context, monitoring is essential as shipwrecks exist in a dynamic equilibrium with their environment and subsequent changes may occur through storm events or impacts of a cultural nature. This is equally valid for sites where active mitigation strategies, such as reburial, have been implemented.

As with the various processes of deterioration, monitoring should consider the two broadly different environments of open seawater and within the seabed. Within the open seawater we are concerned with physical and biological processes of deterioration namely sediment transport (erosion/accretion) and the activity of wood boring organisms. Marine geophysical methods, such as multi beam sonar, can be used to quantitatively assess change over time. In order to study ongoing sedimentary processes, current profilers and sediment sampling (through coring or using sediment traps) can be placed on sites in order to model the likelihood of sediment transport [18]. The presence of actual suspended particulate matter in the water column can also be monitored using turbidity sensors/loggers. This is a relatively simple method of ascertaining if there is sediment transport and in particular when considering the use of the previously described artificial sea grass or netting materials to stabilise a site. In terms of monitoring the presence and activity of wood boring organisms over a site it is, as discussed, not always easy to monitor their activity directly on exposed timbers. However, this can simply be monitored by the placement of sacrificial blocks of modern wood around a site and recording their presence or absence. If they are present it is likely that any newly exposed timbers will also be colonised.

In terms of monitoring within sediments, the dissolved oxygen content, concentrations of various chemical species, porosity and organic content of the sediment can all yield information about the ongoing biogeochemical processes in the sediment and the rate of deterioration of organic matter. These parameters were measured in connection with the Marstrand on the reburial of the *Fredericus* project and full details are given in Gregory [24].

Further to monitoring of the biogeochemical processes, in order to check what is happening to wooden materials, small sacrificial samples of wood should be included as part of a monitoring program as the rate and cause of deterioration can be assessed microscopically in order to confirm biogeochemical monitoring of sediments, as was also carried out in the project [26].

6. Conclusion

Underwater cultural remains, such as wooden shipwrecks, are an unrenewable resource. Those that lie exposed on the seabed can be subjected to deterioration/destruction by human activities such as fishing, construction work and other cultural activities. Furthermore, they can be damaged by the natural effects of climate/weather conditions and underwater currents and biological degradation, which can lead to rapid degradation and their eventual loss. Even under the most favourable conditions, buried in sediments, they under go slow deterioration, which can significantly reduce their strength and integrity.

Therefore, it is of paramount importance that these finds are preserved either by protective methods on the sea bed or through raising and conserving them.

To ensure the survival of the greatest possible number of finds, it is necessary to continue research in order to improve old and develop new methods. For in situ preservation this includes improved assessment of sites and finds; methods to mitigate deterioration, and monitoring techniques. For conservation the main areas to develop and improve are methods for assessing the state of preservation, impregnation agents and drying methods. Regardless of whether a find is preserved in situ or excavated, raised and conserved future methods should not only be technically superior to existing methods, but also quicker and more cost effective, so as to maximize the benefit of our limited resources and secure our cultural heritage for generations to come.

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