Journal of Cultural Heritage 18 (2016) 306–312

Available online at
ScienceDirect
www.sciencedirect.com

Elsevier Masson France
EM|consulte
www.em-consulte.com/en

Original article

Strontium carbonate nanoparticles for the surface treatment of problematic sulfur and iron in waterlogged archaeological wood

Eleanor J. Schofield[a,*], Ritimukta Sarangi[b], Apurva Mehta[b], A. Mark Jones[a], Andrew Smith[c,d], J. Frederick W. Mosselmans[e], Alan V. Chadwick[f]

[a] The Mary Rose Trust, HM Naval Base, The Mary Rose Trust, College Road, HM Naval Base, Portsmouth PO1 3LX, UK
[b] Stanford Synchrotron Radiation Lightsource, Menlo Park, CA 94025, USA
[c] Sci-Tech Daresbury, Keckwick Lane, Daresbury, Cheshire WA4 4AD, UK
[d] Dalton Cumbrian Facility, University of Manchester, Westlakes Science & Technology Park, Moor Row, Cumbria A24 3HA, UK
[e] Diamond Light Source, Didcot OX11 0DE, UK
[f] School of Physical Sciences, University of Kent, Canterbury, CT2 7NH, UK

ARTICLE INFO

Article history:
Received 12 July 2013
Accepted 21 July 2015
Available online 19 August 2015

Keywords:
Waterlogged archaeological wood
Mary Rose
Nanoparticles
Synchrotron spectroscopy
Sulfur
Neutralisation

ABSTRACT

Stabilising waterlogged archaeological wooden artefacts for display presents a challenge for conservators and scientists. Sulfur compounds, incorporated into the wood prior to excavation, can lead to acid formation when exposed to oxygen, and in the presence of iron ions. Strontium carbonate nanoparticles have recently been shown to reduce the production of acid formation at the root by reacting with inorganic sulfur-containing compounds. Here, we show the feasibility of using this treatment on small samples where consolidating treatments have already been performed. It is found that PEG 200 does not prevent the reactivity of the nanoparticles with the sulfur compounds present in the artefacts. A surface brushing application method was found to be successful whilst retaining the visual integrity. In addition, it was found that this technique results in the leaching of iron from the surface layers, preventing future build up of acid catalysed by iron compounds.

1. Research aims

To determine whether polyethylene glycol inhibits the desired neutralisation reaction of strontium carbonate with problematic sulfur.

To assess application methods in terms of practicality, time and cost.

2. Introduction

The development of acids within waterlogged archaeological wood has been shown to cause material and structural degradation [1]. An important example is the Swedish warship *Vasa*, which sank on its maiden voyage in the 17th century, and was raised from the Stockholm harbour in 1966 after spending 333 years underwater [2]. After being treated with polyethylene glycol (PEG) to ensure mechanical stability, the ship was displayed in Stockholm in 1990. After a humid summer, 10 years later, exposed timbers displayed evidence of chemical instability in the form of sulfur-containing precipitates on the surface. To understand the origin of the sulfur, an innovative investigation was undertaken using X-ray absorption near edge spectroscopy (XANES), as it is the only method for quantitative sulfur speciation analysis [3]. It confirmed that sulfate-containing compounds had formed on the timbers in low pH conditions, indicating a highly acidic environment [4].

The lack of oxygen when wood is buried under the seabed or submerged in anoxic seawater slows or prevents the occurrence of several biological and chemical reactions. However, sulfur reducing bacteria thrive under these conditions and continue to react with sulfate ions, which are abundantly available in seawater, leading to the formation of gaseous hydrogen sulfide. Hydrogen sulfide can easily diffuse through the open network structure of waterlogged wood, with enhanced pathways due to water/bacterial erosion and fungal attack. Iron ions are commonly available in waterlogged archaeological wooden artefacts from the corrosion of fixtures (bolts and nails) in the seawater and therefore a large quantity of this reduced sulfur is accumulated in iron based sulfides.

* Corresponding author.
E-mail addresses: e.schofield@maryrose.org (E.J. Schofield), ritis@slac.stanford.edu (R. Sarangi), mehta@slac.stanford.edu (A. Mehta), m.jones@maryrose.org (A.M. Jones), Andy.smith@manchester.ac.uk (A. Smith), fred.mosselmans@diamond.ac.uk (J.F.W. Mosselmans), a.v.chadwick@kent.ac.uk (A.V. Chadwick).

http://dx.doi.org/10.1016/j.culher.2015.07.013
1296-2074/

Whilst submerged in anoxic conditions, these reduced sulfur compounds pose little threat to the stability of archaeological wood. However, upon excavation the reduced sulfur compounds oxidise [4]. The extent of oxidation can vary, and many intermediate oxidised products can be formed, but ultimately most of them transform to sulfates and in the process generate hydrogen ions and therefore an acidic environment. In the presence of water, oxidation of reduced sulfides almost always results in the formation of sulfuric acid. Even when insufficient amounts of water/moisture are present during oxidation to form sulfuric acid, metal (e.g. iron) sulfates can form.

The *Mary Rose*, the 16th century flagship of Henry VIII, sank in the English Solent during an encounter with the French in 1545. After sinking, the ship came to rest on the seabed on its starboard side, which was gradually covered in silt, as the port side eroded away. The silt protected this section of the hull until discovery and subsequent excavation in 1982 [5,6]. Although ostensibly intact, the *Mary Rose* was in an environment that promoted production of reduced sulfur compounds for over 400 years. Therefore, alongside the *Vasa* and many other archaeological organic artefacts, the *Mary Rose* is threatened by the formation of acids and salts, which can destroy the integrity of the wood structure.

In order to develop suitable conservation treatments for sulfur-containing waterlogged archaeological wood, it is critical to determine the sulfur compounds that are present in the artefact. Sulfur K-edge X-ray absorption near edge spectroscopy (XANES) has been pivotal in this work. From XANES analysis we know that the *Vasa* and the *Mary Rose* now contain a variety of sulfur compounds from reduced organic/inorganic sulfur compounds to oxidised sulfate compounds, including many partially oxidised phases [4,7,8]. The extent to which the reduced sulfur compounds would have oxidised whilst underwater is now impossible to determine. However, it is presumed to be minimal due to limited availability of dissolved oxygen available under the seabed.

Previously, mixtures of soda and bicarbonate [9] have been used to neutralise the acidic environment, which does not address the problem of additional acid formation from imminent oxidation of reduced sulfur compounds. In order to devise a long-term conservation strategy, the various degradation issues must first be qualified; the most imminent threat is the acidic environment currently degrading the wood structure followed by the potential long-term threat of oxidation of the reduced sulfur compounds (catalysed by the presence of iron ions), leading to further acidification. To address this issue, the removal of iron from the wood has been attempted using suitable chelating agents [10,11]. However, these chelating agents are expensive and the small residual amount of iron and problematic sulfur which remain, could eventually form acids.

A method to neutralise the sulfur compounds within the wood, would eliminate the possibility of acid formation and ensure long-term stability. Over recent years various nano-scale conservation treatments have been developed, such as nanolimes for conserving limestone artefacts [12,13], nanogels for cleanings works of art [14,15] and nanoparticles for the protection of cultural heritage canvas's and paper [16,17]. Alkaline earth metal hydroxides, such as calcium hydroxide and magnesium hydroxide, have been shown to neutralise acids in waterlogged archaeological wood and produce alkaline reservoirs of calcium carbonate. These reservoirs remain as a future way of neutralising acids [18–20]. However, the sulfate compounds produced still exhibit solubility, and reduced sulfur compounds remain which could eventually oxidise, and neutralise the alkaline reservoir. Strontium carbonate nanoparticles are an alternative reagent which can stabilise sulfates to the relatively insoluble strontium sulfate, and also facilitate the oxidation of reduced inorganic sulfur species, such as pyrite, to strontium sulfate [21], by providing a mildly basic environment. Therefore, immediately eliminating imminent and long-term threats of acid attack from inorganic sulfur compounds.

The lack of practical information and published case-studies hinders the application of this treatment by the conservation community. Another significant concern is the compatibility of the nanoparticles with previous treatments. Depending on the degradation of the wood, due to chemical or biological erosion, consolidants are often incorporated into the wood to achieve long-term mechanical stability. Since their raising, both the *Mary Rose* and the *Vasa* and their associated artefacts have been treated with PEG [2,22]. PEG impregnation being the most commonly used method for archaeological wood worldwide. Assessing whether the nanoparticles can react in this medium is essential and has not been evaluated to date. In previous work completed on *Vasa* timbers, the PEG was removed prior to nanoparticle treatments which is not feasible in an everyday conservation environment due to time, resources and most importantly the stress placed on the wood structure when subjected to cycling of aqueous treatments [19]. Previous work on *Mary Rose* timbers used samples which had not been treated with PEG. In addition, a practical and realistic application method must be determined, which would be accessible in a general working conservation laboratory and within the typical available budget. We therefore aim to determine the feasibility of strontium carbonate nanoparticle treatments for waterlogged wooden archaeological treasures such as the *Mary Rose* and her many artefacts. If successful, this could open the door for the use of nanoparticle treatments for other waterlogged archaeological organic materials.

3. Material and methodologies

3.1. Artefact information

Oak samples from *Mary Rose* artefacts were used in this experiment and are summarised in Table 1. The first samples were from

Table 1
Overview of samples used in the study.

Sample ID	Description	Wood type	Size	PEG treatment	$SrCO_3$ application method
A	Unidentified *Mary Rose* wooden object–section	Oak	1 × 1 × 1 cm	None	None
B	Unidentified *Mary Rose* wooden object–section	Oak	1 × 0.5 × 0.05 cm	None	Immersed in sonicated solution of 0.01 M $SrCO_3$ in iso-propanol
C	Unidentified *Mary Rose* wooden object–section	Oak	1 × 0.5 × 0.15 cm	PEG 200 (20%)	Immersed in sonicated solution of 0.01 M $SrCO_3$ in iso-propanol
D	*Mary Rose* hand weapon	Oak	4 × 4 × 20 cm	PEG 3400 (20%)/6000 (surface treatment)	Sprayed with sonicated solution of 0.01 M $SrCO_3$ in iso-propanol Brushed with $SrCO_3$ and H_2O slurry (1 g in 50 mL)