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Published in:

Proc. 11th ICOM-CC Group on Wet Organic Archaeological Materials Conf., Greenville, USA, May 24-29, 2010, K. Straetkvern and E. Williams (Eds.)

2010

[Link to publication](#)

Citation for published version (APA):

Elding, L. I. (2010). VASA - Recent Preservation Research. In *Proc. 11th ICOM-CC Group on Wet Organic Archaeological Materials Conf., Greenville, USA, May 24-29, 2010*, K. Straetkvern and E. Williams (Eds.) (pp. 371 - 382)

Total number of authors:

1

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Vasa – Recent Preservation Research

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Abstract

The multi-disciplinary work within the research programs *Preserve the Vasa* (2003-2006) and *A Future for Vasa* (since 2008) is reviewed. Objectives are: to further develop the fundamental understanding of the processes occurring in marine archaeological wood and their influence on wood mechanical properties, to elucidate the time dependencies of chemical and mechanical degradation processes and to slow them down or, if possible, stop them. The ultimate goal is to suggest improved methods for practical preservation work based on this research. In this work, differentiation between the hull of 900 tons and the several thousand loose objects has to be considered. Current degradation processes in wood and conservation agent are catalyzed by iron compounds and depend on pH and access to atmospheric oxygen and humidity. Methods to remove iron, neutralize acids, exclude oxygen, adjust physical parameters such as support structure, temperature, relative humidity and light are discussed. A bibliography of the research papers produced in these programs so far is given.

Key Words: Vasa, wood, PEG, sulfur, iron, oxalic acid, sulfuric acid, formic acid, oxygen, humidity, degradation, microbial, Fenton, free radical, acid hydrolysis, oxidative degradation.

Introduction

The history, rescue operations and archaeology of Vasa have been extensively reviewed, most recently by C.O. Cederlund and F. Hocker [1]. The ship sank, fully equipped, on its maiden voyage out of Stockholm in August 1628, after having sailed less than one nautical mile. Salvage attempts during the following decades were fruitless. Only the bronze cannons were recovered in reckless diving operations during the 1660s. The shipwreck was relocated on the bottom of Stockholm harbor during the 1950s and was raised to the surface in 1961.

The hull was spray treated with aqueous PEG solutions between 1962 and -79, dried for another ten years, and moved to the present museum in 1988. Loose objects were PEG-conserved in tanks. The conservation has been described by Barkman [2] and Håfors [3-7, 66]. Emma Hocker has recently given an excellent review of the conditions of the ship and the early preservation research [8]. The absence of shipworm in the brackish waters of the Baltic Sea, the anaerobic conditions in the bottom sediments and the low temperature 30 m below the surface, contributed to the preservation of the ship and loose objects during the 333 years on the seabed. Several tons of iron compounds from rusting cannon balls and bolts, and sulfur compounds from the water and polluted effluents from the town impregnated the wood. Attacks by erosion and sulfur-metabolizing microorganisms softened the wood surfaces. During conservation, large amounts of polyethylene glycol and boron compounds were added [7, 66].

During the 30 years of conservation and drying, and the almost 20 years of display under controlled climate conditions in the present museum, the ship and its loose objects have been exposed to atmospheric oxygen and various degrees of humidity. Together with the large quantities of chemicals in the wood, this has created favorable conditions for chemical processes and transport of chemicals. Already during the 1990s, conservators observed acidic salt deposits on the surfaces of some timbers and loose objects [9], indicating transport of chemicals from the interior to the surface.

After the rainy summer of 2000, when the museum climate by far exceeded the recommended relative humidity of 55 ± 5 %, the situation became alarming. A pilot study was initiated, aimed at identifying the chemical composition of the salt outbreaks. X-ray powder diffraction and synchrotron-based spectroscopy (XANES) by Sandström, Persson and coworkers identified the deposits as composed of hydrated iron sulfates, gypsum and elemental sulfur [10-12]. It was concluded that hydrogen sulfide, formed during the anaerobic conditions on the seafloor, had penetrated the submerged wood, accumulated as mainly elemental sulfur, and later, during museum conditions, oxidized to sulfuric acid in iron-catalyzed processes. Wood hydrolysis due to internal sulfuric acid formation was assumed to be a serious matter of conservation concern [10-15]. This pioneering work, summarized in *Nature* [12], formed the basis for much work on the "sulfur problem" during the years to follow. It also was the basis and rationale for the continued and extended research efforts on the processes in Vasa wood during the years to follow. However, it is now (2010) clear that the situation in the timbers is much more complicated than initially assumed ten years ago. Novel results indicate that the original strong focus on the oxidation of sulfur to sulfuric acid has to be modified – this is one of several possible reactions, and several other acids contribute to the acidity of the wood (*vide infra*).

Preserve the Vasa

In the beginning of 2003, the Swedish National Maritime Museums (SMM) received funding for research in the chemical and microbial processes occurring in the timbers of Vasa. At that time, very little was known about the ongoing processes in PEG-treated archaeological wood. It was explicitly stressed that the research should result in a fundamental understanding of these processes as a basis for practical preservation work. The transformation of sulfur compounds either by iron-catalyzed processes involving atmospheric oxygen and humidity, or by activities of sulfur-oxidizing bacteria, was assumed to result in formation of sulfuric acid [12]. The possible degradation of PEG was also a matter of concern. After announcement of this program and review of received proposals, the research program started Oct 1st, 2003 [16].

Microbial activities - Initially, it was considered important to differentiate between chemical and microbial processes. It was known early that the outer regions of Vasa timbers were degraded due to bacterial attacks during the time on the seabed [7]. This fact was confirmed by light microscopy [17] and scanning electron microscopy, showing that the outer ca 1-2 cm of Vasa oak – and more in the case of softwood - was degraded by erosion bacteria. Later, the processes involving erosion bacteria and sulfate-reducing bacteria and the mechanisms for accumulation of organic lignin-bound sulfides and inorganic iron-sulfur compounds under seabed conditions were comprehensively elucidated by Fors et al. in laboratory simulations [18].

As a result of a co-operation between the School of Biology at the University of Portsmouth and the Department of Wood Chemistry at the Swedish Agricultural University, it could relatively soon be concluded – perhaps not too surprising – that microbial activity under the present relatively dry museum conditions was of minor importance, with the exception of the wood surfaces, always exposed to contamination from the public. All samples taken from interior Vasa wood in its present dry state failed to provide any signs of ongoing microbial activity. But the DNA analysis afforded interesting information on the microbial history of the ship and the species present during the wet periods [19-21]. Based on these results, all research and preservation efforts could be concentrated to the chemical processes.

Sulfur and iron chemistry - Speciation and distribution of sulfur and iron compounds in Vasa wood was under intense study by Sandström's group at Stockholm University. It resulted in a number of seminal publications [22-27], including comparative studies of some other ships [23-26]. The novel discovery of accumulation of reduced sulfur as thiols bound to lignin and as solid particles of iron sulfides was found to be of general

occurrence for water-logged marine-archaeological wood recovered from sea water under anoxic conditions. By use of synchrotron-based methods, *i.e.* XANES (X-ray Absorption Near Edge Spectroscopy) and SXM (Scanning X-ray Microscopy) at Stanford and Grenoble, together with X-ray fluorescence, ESCA (Electron Spectroscopy for Chemical Analysis), SEM (Scanning Electron Microscopy) and X-ray powder diffraction, valuable new information on the distribution and speciation of sulfur and iron was obtained. High concentrations of sulfur and iron, in some cases up to 10% by weight, were observed in the bacterially degraded surface regions of Vasa wood down to 1-2 cm. These observations match the results of the simulations of the microbial processes [18].

Iron extraction - At an early stage, removal of the iron impurities was identified as an important remedy to minimize their catalytic action. Extraction methods by use of strong EDTA-related complexing agents (EDDHMA and DTPA) were tested from the start of the project and are described in a number of publications by Persson and Almkvist [28-30]. These extractions require several months of exposure, and the interior of very massive pieces might be inaccessible. The treatment removes all water-soluble compounds including the PEG, and it neutralizes acids, since the pH of the extraction solution is ca 9 in the case of EDDHMA. This means that extracted objects have to be re-conserved. Successful extractions of pine species have been performed [29, 30], and the practical use of DTPA is reported at this conference [31]. Exposure to high pH for prolonged times might be a threat to the cellulose. In the case of Vasa, final decisions and tests of the implications of the method for the wood are still under evaluation and it may be that only the more robust objects will be able to withstand this treatment (*vide infra*).

PEG degradation - Initially, it could not be excluded that degradation of PEG to formic acid, for instance, also contributed to the acidity observed in some Vasa samples. Moreover, the stability of the conservation agent is of great importance *per se*, in that even a very slow decomposition of PEG to shorter fragments is expected to increase the hygroscopicity and impair the efficiency of the PEG stabilization of the impregnated wood. The distribution of PEG in Vasa wood and its stability and degradation mechanisms was therefore studied.

The model molecule tetraethylene glycol and its degradation reactions as a function of temperature and chemical environment, and PEG from Vasa and other ships were analyzed by Glastrup, et al. at the Danish National Museum [32-35]. They conclude that PEG is relatively stable under museum conditions and that formic acid is a possible product of a slow degradation. Recently, Mortensen reviewed and extended these studies in his PhD thesis [36] and in his report to this conference [37]. Based on

carbon-14 experiments, it can be concluded [36, 37] that the observed formic acid is a degradation product of PEG, not a result of a solvolytic degradation of wood as hypothesized earlier [38]. According to these experiments, the half-life of PEG under museum conditions is - in practice – sufficiently long (thousands of years) for all practical purposes.

Parallel to these studies, work by Persson and Almkvist on PEG properties and reactions [39-45] resulted in a partly different picture. The two groups agree that the PEG in the surface region is stable [36, 39]. However, mass spectra of PEG from the interior wood (where PEG concentrations are low) indicate a predominance of low-molecular PEG. Combined with the hypothesis that high concentrations of iron(II) might give rise to Fenton-type free radical attacks on macromolecules in these samples, they conclude that PEG in the interior wood might be degraded due to free radical attack in a random-cleavage process [43-45]. Alternatively, these observations might be interpreted as a result of a chromatographic separation of PEG in the wooden matrix [36]. Summarizing, since the concentrations of PEG in the interior wood are low, and even if there is a degradation of PEG at these low concentrations, the present view of the Vasa Museum authorities is that PEG degradation is not of high priority in the applied preservation work. Further, solvolysis of wood in the presence of acids and PEG according to [38] can definitely be ruled out.

Wood chemistry and stability – During the second phase of the “*Preserve the Vasa*” project, starting early 2005, a comprehensive study of the chemical and mechanical properties of Vasa oak compared to reference wood (fresh wood and waterlogged, non-conserved contemporary oak) was launched. The aim was to answer the most important question for the long-term preservation of the ship: *Is there an ongoing deterioration of the wood under the present museum conditions, i.e. since 1990, weakening the structure, as a result of chemical processes in the timbers?*

Systematic sampling from the ship [17] and analysis of organic acids and other degradation products by NMR and of cellulose and hemicellulose by SEC (Size Exclusion Chromatography) were initiated. The SEC analytical studies by Iversen, et al. [46, 47] indicated that most of the observed degradation of cellulose has occurred after the salvage, most likely as a consequence of the iron contaminated and humid wood being in contact with air, creating possibilities for Fenton-type oxidative degradations and acid-initiated hydrolysis reactions. Similar conclusions were derived by Godfrey, et al. using solid state carbon-13 NMR [48]. pH measurements and proton-NMR data for D₂O extracts of finely divided wood samples by Persson and Almkvist also indicated the presence of organic acids and degradation in the interior wood through the same possible mechanisms. Noteworthy, in the interior wood,

Almkvist observed positive correlations between the occurrence of high concentrations of iron(II) and increasing acidity and signs of degradation of PEG and cellulose [41-45].

Parallel to these chemical studies, a program on the mechanical properties of Vasa wood had been initiated. A study using high-energy multiple impact milling within the Vasa wood project [17] at the University of Hannover indicated degradation but gave no conclusive results [49]. Studies at the Royal Institute of Technology in Stockholm resulted in publications on fundamental physical properties of Vasa wood in comparison with fresh wood and correlations between moisture and PEG content and radial and tangential compression [50-52]. A ca 50% reduction of compressive strength of Vasa oak was derived. There was an obvious need to extend these studies and to correlate the physical properties of Vasa oak with its chemical condition.

Evaluation – The “*Preserve the Vasa*” project was accomplished in 2006-2007 and evaluated in December 2006 [53]. The reviewers recommended phasing out of parts that had accomplished the goals (microbial biology, sulfur spectroscopy, PEG decomposition) and suggested that future research should focus on, for instance, acid formation, mechanisms for oxidative degradations, neutralization methods, wood mechanical properties and practical applications [53].

A Future for Vasa

A research plan for *A Future for Vasa* was formulated based on the knowledge of 2007 and the reviewer’s recommendations [53], including the following main objectives:

- Understand and if possible arrest the decay processes occurring in Vasa wood
- Elucidate the time dependence of these processes
- Clarify the relations between the chemical status of the wood and its physical-mechanical properties
- Elucidate the effect of PEG conservation on long-term wood mechanical properties
- Apply research results in new methods for practical preservation work, including a new support structure
- Elucidate consequences of re-conservation compared to the effects if no such actions are taken
- Investigate possibilities of future non-destructive monitoring of ship and loose artifacts

The project received funding from Swedish research foundations in 2008. It was launched in October 2008 and is scheduled for 3 years. At present five research laboratories are involved. A short summary of current activities is as follows:

Wood chemical properties – The analytical work by Iversen, et al. [46, 47] on authentic Vasa wood referred to above, indicates that cellulose degradation also occurs in the interior wood. Comparison with non-conserved reference wood indicates that degradation has occurred since the material was exposed to air. The relative contribution from oxidative degradation (Fenton chemistry) and acid hydrolysis is still an open question. Based on carbon-13 NMR, Iversen recently reported quite high concentrations of oxalic acid in the interior wood, in addition to the formic and acetic acids present. Since this is a strong acid (pKa 1.3) it may contribute to the over-all acidity and to hydrolysis of cellulose.

Similarly, the work by Persson and Almkvist [41-45] indicates degradation in the inner parts of the wood. The positive correlation between high iron(II) concentrations and degradation [41] most likely speak in favor of an oxidative degradation. Noteworthy, samples containing rather high concentrations of sulfur in addition to the iron show less degradation [42]. This is an important observation; it might be interpreted as a possible inhibition of free radical processes by reduced sulfur compounds acting as scavengers. Thus, the original hypothesis [12] of a sulfuric acid mediated acid hydrolysis of the cellulose as the main degradation mechanism seems to be an over-simplification. Other processes and other acids might be equally - or most likely more - important. Reactions depending directly or indirectly on the iron(II/III) redox chemistry are definitely key processes.

Intensified studies of oligosaccharide decay products and lignin status of Vasa wood is in progress in co-operation with the Department of Wood Technology at the Royal Institute of Technology (KTH) in Stockholm. The aim is to retrieve more information of importance for the determination of degradation reaction mechanisms.

Accelerated ageing – Almkvist, in co-operation with Ingela Bjurhager at the Royal Institute of Technology (KTH), has launched a series of model experiments, reported at this meeting [54]. Fresh oak is exposed to iron compounds, PEG and various oxygen pressures, relative humidities and temperatures. Interestingly, the conditions of authentic Vasa wood can be reproduced quite well, and the ageing experiments indicate that the degradation is rather rapid initially and then decelerates to become rather slow. The chemically treated model samples are subjected to mechanical testing as described below in order to establish relations between chemical status and mechanical properties.

Wood mechanical properties – The early work at the Fibre and Polymer Technology department at KTH referred to above [50-52] is continued. Bjurhager has devised methods for determination of mechanical properties of hardwoods and PEG-impregnated waterlogged wood [55, 56]. Axial tension of Vasa oak as well as fresh oak treated in the accelerated ageing experiments are determined [54]. There is a good correlation between the observed tensile strength and the degradation status of these samples. Thus, a relatively good mechanical stability is observed in the wood below the soft bacterially degraded PEG-rich surface region. But further inside the timbers, the mechanical properties again get worse, in agreement with the chemical results indicating degradation processes in this region. Current results indicate a decrease of mechanical strength of Vasa wood compared to fresh oak of ca 30 %. Further work in this field will include compression tests.

Reaction rates – Most chemical reactions in archaeological wood consume oxygen, directly or indirectly. Oxygen consumption rates can be used to determine reaction rates [57]. In a co-operative project with Matthiesen and Mortensen at the Danish National Museum oxygen consumption and diffusion in Vasa wood is being studied, as reported at this meeting [58]. Diffusion rates in wood vary depending on the properties of the particular sample, but oxygen concentrations inside wood are lower than in the atmosphere, indicating oxygen consumption inside wood. Iron(II) impregnated samples consume more oxygen, indicating an iron(II) catalyzed process.

Implementation

It was early recognized that different treatment methods are needed for the hull of 900 tons and the ca. 20 000 loose wooden artifacts. The hull can hardly be treated with wet-chemical or gas methods in the presence of the public. Closing the museum during a couple of years for extensive re-conservation operations is not realistic. Vasa attracts more than 1 million visitors annually and - under all circumstances - the museum authorities want the ship and the collections to be exposed in a visitor-friendly manner.

Thus, the climate will be the most important parameter. In 2004, a new climate system was installed, which has proven capable of keeping RH and temperature under very good control, independent of the number of visitors and the outdoor climate, as reviewed by E. Hocker [59]. The question is how low the temperature and – in particular – the RH can be taken without detrimental effects. As a result of the very stable climate, salt deposits resulting from transport of humidity inside the timbers have decreased in number and occurrence [60].

Another important parameter is the support structure. The ship is now resting on the original keel blocks and supporting elements installed in 1964 with some provisional improvements. A geodetic positional system indicates that the hull is moving very slightly. A plan for a better support system has to take into consideration the rates of the chemical degradation processes and the accompanying mechanical weakening of the timbers, since a new support system should be dimensioned to last for many decades.

Several methods are now available for treatment of loose objects. The iron extraction method, which is also a neutralization method, works well with the exception of very thick timbers, whose interior is inaccessible. But the long-term effects on the wood caused by the strongly basic extraction solutions are still a matter of uncertainty. Further experiments to investigate the practical parameters are now in progress in cooperation with the Swedish National Heritage Board.

Other wet-chemical neutralization methods involving nano particles of calcium or magnesium hydroxides with propanol as carrier solvent also seem to work well and have been tested on Vasa material [61-63], but the penetration depth remains to be studied. The original – and detrimental - method of neutralization with poultices soaked with sodium bicarbonate suggested early [9, 11, 13] was fortunately discontinued in 2005. In general, use of wet chemical methods means that all soluble substances are removed and re-conservation is necessary.

Treatments with gaseous ammonia have been tested on Vasa material [64, 65]. The penetration of the gas is limited to 5-10 mm from surface, *i.e.* only to the bacterially degraded regions. Since current research indicates degradation processes and acidic conditions at greater depths, the method is probably not useful in practical preservation work. Its use will be impossible for the hull. Common to all neutralization methods is that they will inhibit not only acid degradation processes, but also Fenton-type free radical processes, which require pH values below ca 4.

The research work shows that oxygen is necessary for the degradation processes. Keeping valuable objects under inert gas after extraction or neutralization treatment followed by re-conservation by PEG treatment and freeze drying would be one safe method for long-lasting preservation.

One very important parameter, still unknown, is the rate and extent of the observed degradation processes. Model experiments by accelerated ageing might give some information but are inherently difficult to interpret. Authentic Vasa material has now been under inspection with state-of-the-art experimental techniques for nine years.

This period is probably too short to allow for estimation of the slow rates involved – one decade might only represent one point on the on a very long time axis. On several occasions researchers have been asking for samples representing the wood status say, at the time of salvage in 1961, when conservation was finished in 1979, or when the ship entered the new museum in 1988. Such samples are not available. Probing Vasa today and saving these samples for a couple of decades under anaerobic conditions at low temperature would enable researchers of future generations to compare these samples with the status of the timbers kept under normal museum conditions. Such strategy would admit better estimations of the changes of wood properties over time.

It is desirable to keep sampling of wood at a minimum, both with respect to number and size. Plans for shared use of samples by several research groups and non-destructive methods, such as ultrasound, are under consideration. Noteworthy, different methods of treatment will be necessary for different groups of objects depending on for instance degradation status, wood species and cultural-historical value. This is a matter of present evaluation.

Acknowledgements

The Swedish National Maritime Museums' research programs "*Preserve the Vasa*" and "*A Future for Vasa*" were financially supported by The Swedish Research Council (VR), The Swedish Foundation for Strategic Research (SSF), The Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (FORMAS), The Swedish Agency for Innovation Systems (VINNOVA), The Bank of Sweden Tercentenary Foundation and the Swedish National Heritage Board. This support is gratefully acknowledged.

Note added in proof

Since this meeting, a PhD thesis by B. Håfors on the conservation of Vasa and the PEG conservation programs used has appeared (66).

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