Ten Years of VASA Research - Review and Outlook

Elding, Lars Ivar

Published in:
Proc. Int. Conf. Shipwrecks 2011, Roy. Inst. of Technology, KTH, Stockholm, Oct 18-21, 2011, M. Ek (Ed.)

2011

Citation for published version (APA):
Elding, L. I. (2011). Ten Years of VASA Research - Review and Outlook. In *Proc. Int. Conf. Shipwrecks 2011, Roy. Inst. of Technology, KTH, Stockholm, Oct 18-21, 2011, M. Ek (Ed.) : Chemistry and Preservation of Waterlogged Wooden Shipwrecks* (pp. 86 - 93).

Total number of authors:
1

KTH Chemical Science and Engineering

Proc. Int. Conf. Shipwrecks 2011, 18-21 Oct 2011, Roy. Inst. of Technology, Stockholm, Monica Ek, Ed., ISBN 978-91-7501142-4, pp. 86-93

TEN YEARS OF VASA RESEARCH – REVIEW AND OUTLOOK

Lars Ivar Elding

The Vasa Museum, POB 27 131, SE-102 52, Stockholm, and Department of Chemistry, Lund University, POB 124, SE-221 00 Lund, Sweden, larsi.elding@inorg.lu.se lars-ivar.elding@maritima.se

INTRODUCTION

VASA sank in 1628 in Stockholm harbor during her maiden voyage. The shipwreck was relocated during the 1950s and was raised to the surface in 1961 [1]. The absence of shipworm in the brackish waters of the Baltic Sea, the anaerobic conditions and low temperature in the bottom sediments 30 m below the surface contributed to its preservation. Several tons of iron compounds from rusting cannon balls and iron bolts and sulfur compounds from the water and polluted effluents from the town impregnated the wood. Erosion bacteria attacked the wood surfaces. During conservation 1962 to 1979, the hull was treated with aqueous polyethylene glycol (PEG) solutions and then dried for another ten years. Loose objects were PEG conserved in tanks. Large amounts of PEG and boron compounds were added to the timbers in this process [2]. Since 1989, the ship and its collections are kept under controlled climate conditions in the present museum.

During the 50 years since 1961, the ship has been exposed to atmospheric oxygen and various degrees of humidity, which has created favorable conditions for chemical and biological degradation processes and transport of chemicals in the wood. During the 1990's, conservators observed acidic salt deposits on the surfaces of some timbers and loose objects [3], indicating transport of chemicals from the interior to the surface. After a rainy summer in 2000, when the museum climate by far exceeded the recommended relative humidity values, the situation became alarming. The salt outbreaks were identified as hydrated iron sulfates, gypsum and elemental sulfur [4]. It was concluded that hydrogen sulfide in the timbers, formed during the anaerobic conditions on the seafloor, was oxidized under museum conditions to sulfuric acid in iron-catalyzed processes. Degradation of the wood due to the action of sulfuric acid was an obvious threat [3,4]. This pioneering work is the basis and rationale for the comprehensive research efforts on the processes in the wood of Vasa and other ships during recent years.

RESEARCH PROJECTS

PRESERVE THE VASA

In 2003, research on the chemical and microbial processes occurring in the timbers of Vasa was initiated. Little was then known about the nature of these processes in PEG-treated archaeological water-logged wood. The research aimed at a fundamental understanding as a basis for practical preservation work. The transformation of sulfur compounds to sulfuric acid, either by iron-catalyzed reactions involving atmospheric oxygen and humidity, or by action of sulfur-oxidizing bacteria, and the possible degradation of PEG, should be elucidated.

Microbial activity - It was soon concluded that microbial activity during the prevailing dry museum conditions was of minor importance. Samples taken from interior Vasa wood failed to provide any signs of current microbial activity. But DNA analysis afforded interesting information on the microbial history of the ship and the species present during the wet periods [5]. Based on these results, all research and preservation efforts were concentrated to the chemical processes. 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 elucidated in laboratory simulations [6].

Sulfur and iron chemistry - Studies of speciation and distribution of sulfur and iron compounds in Vasa and some other ships by use of synchrotron-based methods, *i.e.* XANES (X-ray Absorption Near Edge Spectroscopy) and SXM (Scanning X-ray Microscopy), together with X-ray fluorescence, ESCA, SEM and X-ray powder diffraction showed accumulation of reduced sulfur as thiols bound to lignin and as iron sulfide particles [7-9]. High concentrations of sulfur and iron, in some cases up to 10% by weight, were observed in the bacterially degraded surface regions down to 1-2 cm [7-9].

Iron extraction - Removal of iron impurities was identified as important to minimize their assumed catalytic action. Extraction by use of sequestering agents (EDDHMA and DTPA) was initiated early [10]. The washing out of iron requires long exposure times, and the interior of massive oak pieces is in practice inaccessible for wet chemical methods. The treatment removes water-soluble compounds including PEG, and it neutralizes acids, since the aqueous extraction solutions are alkaline. Extracted objects have to be re-conserved. Successful extractions of pine species have been performed [10].

PEG degradation - Initially, it could not be excluded that degradation of PEG to for instance formic acid also contributed to the observed acidity. Studies of the distribution of PEG in Vasa wood and its stability and degradation mechanisms indicated that the half-life of PEG under museum conditions might be sufficiently long (thousands of years) for all practical purposes [11,12]. It was hypothesized, however, that PEG in the interior wood might degrade due to free radical attack [13-16]. The stability of the conservation agent is of great importance *per se*, in that even a very slow decomposition of PEG to shorter fragments will increase the hygroscopicity and impair the efficiency of the PEG stabilization.

Wood chemistry and stability - 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 in 2005. The aim was to answer the most important question for the long-term preservation of the ship: *Is there a continuous decrease of the mechanical properties of the wood under present museum conditions, as a result of chemical processes in the timbers?*

Analysis of organic acids and other degradation products by NMR and of cellulose and hemicellulose by Size Exclusion Chromatography (SEC) [17] indicated that most of the observed cellulose degradation most likely has occurred after the salvage as a result of the iron rich and humid wood being exposed to air, creating possibilities for oxidative degradations and/or acid-initiated hydrolysis reactions. pH measurements and proton-NMR data for D_2O extracts of finely divided wood samples also indicated the presence of organic acids and degradation in the interior [16]. Positive correlations between high concentrations of iron(II), increasing acidity and signs of degradation of PEG and cellulose were observed [13-16].

In parallel to these studies, a program on the mechanical properties of Vasa wood was initiated, including measurements of fundamental physical properties of Vasa wood in comparison with fresh wood and of correlations between moisture and PEG content and radial and tangential compression [18-19]. A reduction by ca 50% of compressive strength of Vasa oak compared to fresh oak was derived. There was an obvious need to further extend these wood mechanical studies and to correlate the physical properties of Vasa oak with its chemical condition.

A FUTURE FOR VASA

Based on conclusions from the *“Preserve the Vasa”* project [20], *A Future for Vasa* was launched in 2006, with 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 to new methods for practical preservation work, including a new support structure
- Elucidate the consequences of re-conservation compared to the effects, if no such actions are undertaken
- Investigate possibilities of future non-destructive monitoring of ship and loose artifacts

Wood chemical properties – Analysis of Vasa wood indicates that cellulose degradation also occurs in the interior wood [14-17]. Comparison with non-conserved reference wood indicates that degradation has occurred since the Vasa wood was exposed to air [17]. Based on carbon-13 NMR, high concentrations of oxalic acid in the interior wood was observed. This is a strong acid (pKa 1.3) that will initiate hydrolysis of cellulose. The relative contribution from oxidative degradation (Fenton chemistry) and hydrolysis due to oxalic acid is still an open question. Interior wood samples containing rather high concentrations of sulfur in relation to iron show less degradation [14-16]. This has been interpreted as a possible inhibition of free radical processes by reduced sulfur compounds acting as scavengers [16].

To conclude, the original hypothesis [4] of a sulfuric acid mediated hydrolysis of cellulose might be important in the bacterially degraded sulfur-rich surface regions. However, the cellulose/hemicellulose is already depleted there due to bacterial degradation. In the interior wood, sulfur concentrations are low and other processes and other acids are probably more important. Attempts to neutralize acids in Vasa wood by nanotechnology [21] or ammonia gas treatment [22] have been performed with some success.

Accelerated ageing – Model experiments in which fresh oak is exposed to iron compounds, PEG and various oxygen pressures and temperatures have been reported [15]. The conditions of authentic Vasa wood can be reproduced quite well, and the experiments indicate that the degradation is rather rapid initially and then decelerates to become rather slow. The chemically treated model samples have been subjected to mechanical testing in order to establish relations between chemical status and mechanical properties.

Wood mechanical properties – Based on the early work [18-19], methods for determination of mechanical properties of hardwoods and PEG-impregnated waterlogged wood have been further developed [23-25]. Axial tension of Vasa oak as well as fresh oak treated in accelerated ageing experiments have been determined by use of miniaturized samples. There is a good correlation between the observed longitudinal tensile strength and the chemical degradation status as expressed by the average molecular weight. 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 get worse, in agreement with the chemical results indicating interior degradation processes. Current results indicate a decrease of mechanical strength of interior Vasa wood compared to fresh oak of up to ca 50 %, sometimes even more [25]. The lignin status of Vasa wood, on the other hand, is not very different from fresh wood.

Reaction rates – Most chemical reactions in archaeological wood consume oxygen, directly or indirectly. Oxygen consumption rates can be used to determine reaction rates. Oxygen consumption and diffusion in Vasa wood has been studied [26]. Diffusion rates in wood seem to be fast, and concentrations inside wood are lower than in the atmosphere, indicating interior oxygen consumption. Iron(II) impregnated samples consume more oxygen, indicating possible iron(II) catalyzed processes.

CONCLUSIONS AND PERSPECTIVES

Microbial activity under the present dry conditions is negligible, but was important during the time on the seabed and possibly also during the wet phases of the conservation; previously active microbial species have been identified by DNA and RNA analysis. Current cellulose degradation is caused by chemical processes, involving sulfur and iron compounds in combination with the humidity of the wood and atmospheric oxygen. The degradation chemistry consumes oxygen, and methods for measurement of oxygen consumption in wood have been developed. Acidic salt deposits on wood surfaces, indicating transport of chemicals from the interior to the surface, have been characterized and the mechanism for their formation has been studied in climate chamber experiments. Speciation and distribution of sulfur and iron compounds in the timbers has been elucidated in detail. High concentrations of sulfur and iron in the bacterially degraded surface regions of the timbers, in some cases up to 10% by weight, favor sulfuric acid dependent hydrolysis of cellulose in this region. Deep below the surface, sulfuric acid concentrations are negligible, and cellulose degradation as observed by means of size exclusion chromatography and axial tension measurements might be due to free radical reactions of Fenton type and/or acid hydrolysis caused by other acids, in particular oxalic acid. A positive correlation between the mechanical weakening and the extent of chemical degradation as expressed by average molecular weight is observed. Chemical degradation and mechanical weakening are important also in the deep interior of the timbers. The long-term changes of the complex wooden structure of the ship are monitored by use of a precise geodetic positional system in the museum. The observed changes so far are slow and most probably also not linear over time.

Still unknown key parameters are the exact nature of the various possible chemical degradation reactions, their individual rates and their relative contributions to the over-all ageing of the wooden material. These basic data will affect the expected life-time of the ship. Attempts to determine the time dependence of the chemical processes by oxygen consumption measurements are not conclusive due to the heterogeneity of the material. Simulation experiments of the time-dependent changes of the real material by accelerated ageing experiments on fresh oak exposed to various well-defined chemical treatments have given some information, but are inherently difficult to interpret. The origin of the high concentrations of oxalic acid observed in the interior wood is also not clear.

Methods for evaluation of the precise nature and rate of the chemical degradation processes have to be further developed, as well as methods to stop or at least decelerate these processes under museum conditions. The occurring chemical processes are inherently slow, and there is a big problem in determining their absolute rates. An alternative to accelerated ageing or oxygen consumption measurements would be to quench reactions for a long period of time by low temperature and inert gas for future analysis, comparing the result with wood aged under museum conditions.

The heavy ship construction is subject to gravitational forces and its long-term preservation and stability will depend on the mechanical properties of the wooden construction details and their change with time. These in turn depend on the chemical degradation status, and the time dependence of the chemistry. Since this is still not sufficiently well known, the rate of the mechanical weakening of the hull is also not known. Moreover, mechanical properties have been determined on a microscopic level. To be practically useful, this knowledge has to be extrapolated to the complex, heterogeneous and heavy hull structure, which is not a trivial operation.

Quantitative evaluation of the correlations between the chemical processes and the mechanical properties of the wood has to be further developed. The recorded microscopic mechanical properties have to be extrapolated to the properties of macroscopic timbers and the complex hull structure and have to be supported by systematic observations of the movements of the hull structure and with complementary experiments on creep properties of wood species under well defined loads. Computer simulations involving finite element methods will be important for decisions on future actions to support the hull.

Wet chemical methods for neutralization of acids, removal of iron compounds and preventing free-radical processes should be further developed, as well as gas treatments for neutralization or for exclusion of atmospheric oxygen, in particular for loose objects. For the hull, environmental parameters such as relative humidity, temperature, light, and support structure have to be optimized. A Hi-tech climate system in the museum is a necessity for successful preservation.

In a more general context, future development of novel conservation and stabilization agents should be of high priority. These could be based on spontaneous assembly to supramolecular structures, and be given properties allowing neutralization of acids, free-radical capture or complexation of detrimental metal ions. This will be an important field for future advanced research in organic synthesis and supramolecular chemistry. Chemical analysis of archaeological wood, based on a wide spectrum of instrumental methods, has been successfully developed during the last 15 years and has afforded a lot of novel information. New technologies that might offer further possibilities for elucidation of the status of archaeological wood might involve fast laser spectroscopy, ultrasound studies, neutron diffraction and X-ray scattering.

ACKNOWLEDGEMENTS

Financial support from 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, the Swedish National Heritage Board and K.& A. Wallenberg foundation is gratefully acknowledged.

SELECTED REFERENCES

1. C.O. Cederlund, *Vasa I. The Archaeology of a Swedish Warship of 1628*. F. Hocker (ed), The National Maritime Museums of Sweden, Stockholm 2006.
2. B. Håfors, *Conservation of the Wood of the Swedish Warship Vasa of A.D. 1628*. PhD thesis, Gothenburg University, 2011.
3. T.P.A. Sandström, I. Hall-Roth and A. Karlsson, *Salt precipitation on Vasa Timbers: An Introduction to a Problem*, in *Proc. 8th ICOM-WOAM Conf.*, Stockholm 2001, P. Hoffmann, J.A. Spriggs, T. Grant, C. Cook, A. Recht (eds.) Bremerhaven 2002, 55-66.
4. M. Sandström, F. Jaliehvand, I. Persson, U. Gelius, P. Frank and I. Hall-Roth, *Deterioration of the sevententh-century warship Vasa by internal formation of sulfuric acid*, in *Nature*, 415, 2002, 893-897.
5. S. Hotchkiss, E. Landy, K.-L. Pang and J. Mitchell, *Bacteria in Archaeological Waterlogged Wood: Molecular Protocols for Diversity and Community Studies*, in *Heritage, Microbiology and Science*, E. May, M. Jones, J. Mitchell (eds), Roy. Soc. Chem. Special publ. No. 135, Cambridge 2008, 108-127.
6. Y. Fors, T. Nilsson, E. Damian Risberg, M. Sandström and P. Torssander, *Sulfur accumulation in pine wood induced by bacteria in a simulated seabed environment: Implications for marine archaeological wood and fossil fuels*, in *Int. Biodeterioration & Biodegradation*, 62, 2008, 336-347.
7. M. Sandström, F. Jaliehvand, E. Damian, Y. Fors, U. Gelius, M. Jones and M. Salomé, *Sulfur accumulation in the timbers of King Henry VIII's warship Mary Rose: A pathway in the sulfur cycle of conservation concern*, in *Proc. Nat. Acad. Sci. USA*, 102 (40) 2005, 14165-14170.
8. Y. Fors and M. Sandström, *Sulfur and iron in shipwrecks cause conservation concerns*, in *Chem. Soc. Rev.,* 2006, 35, 1-17.
9. Y. Fors, *Sulfur-Related Conservation Concerns for Marine Archaeological Wood*, PhD thesis, Stockholm University, 2008.
10. G. Almkvist and I. Persson, *Extraction of iron compounds from wood from the Vasa*, in *Holzforschung,* 60(6), 2006, 678-684.
11. M.N. Mortensen, H. Egsgaard, S. Hvilsted, Y. Sashoua and J. Glastrup, *Characterization of the polyethylene glycol impregnation of the Swedish warship Vasa and one of the Danish Skuldelev Viking ships*, in *J. Archaeol. Sci*., 34(8), 2007, 1211-1218.
12. M. N. Mortensen, *Stabilization of polyethylene glycol in archaeological wood*, PhD thesis, Technical university of Denmark and National Museum of Denmark, Lyngby 2009.
13. G. Almkvist and I. Persson, *Degradation of polyethylene glycol and hemicellulose in the Vasa*, in *Holzforschung,* 62(2), 2008, 64-70.
14. G. Almkvist and I. Persson, *Analysis of acids and degradation products related to iron and sulfur in the Swedish warship Vasa*, in *Holzforschung*, 62(6), 2008, 694-703.
15. G. Almkvist and I. Persson, *Fenton-induced degradation of polyethylene glycol and oak holocellulose. A model experiment in comparison to changes observed in conserved waterlogged wood*, in *Holzforschung*, 62(6), 2008, 704-708.
16. G. Almkvist, *The Chemistry of the Vasa – Iron, Acids and Degradation*, PhD thesis, Swedish University of Agricultural Sciences, Uppsala 2008.
17. E.L. Lindfors, M. Lindström and T. Iversen, *Polysaccharide degradation in water-logged oak wood from the ancient warship Vasa*, in *Holzforschung*, 62(1) 2008, 57-63.
18. J. Ljungdahl, L.A. Berglund and M. Burman, *Transverse anisotropy of compressive failure in European oak. A digital speckle photography study*, in *Holzforschung*, 60(2), 2006, 190-195.

19. J. Ljungdahl and L.A. Berglund, *Transverse mechanical behavior and moisture of waterlogged archaeological wood from the Vasa ship*, in *Holzforschung*, 61(3), 2007, 279-284.
20. A. McAuley, B. Holmbom, P. Hoffmann and P. Jensen, *International Evaluation of the Preserve the Vasa Project*, Statens Maritima Museer, Stockholm 2006, http://www.vasamuseet.se/Documents/Bevara%20Vasa%20Utv%c3%a4rdering%202ed.pdf
21. R. Giorgi, D. Chelazzi and P. Baglioni, *Nanoparticles of Calcium Hydroxide for Wood Conservation. The De-acidification of the Vasa Warship*, in *Langmuir*, 21, 2005, 10743-10748.
22. Y. Fors and V. Richards, *The effects of Ammonia Neutralizing Treatment on Marine Archaeological Vasa Wood,* in *Studies in Conservation,* 55, 2010, 41-54.
23. I. Bjurhager, J. Ljungdahl, L. Wallström, E.K. Gamstedt and L.A. Berglund, *Towards improved understanding of PEG-impregnated waterlogged archaeological wood: A model study on recent oak*, in *Holzforschung*, 64(2), 2010, 243-250.
24. I. Bjurhager, *Effects of Cell Wall Structure on Tensile Properties of Hardwood*, PhD thesis, Royal Institute of Technology, Stockholm 2011.
25. I. Bjurhager, H. Nilsson, E.L. Lindfors, T. Iversen, G. Almkvist, K. Gamstedt, L.A. Berglund, *Significant loss of mechanical strength in archaeological wood from the 17th century Vasa ship – correlation with cellulose degradation*. Manuscript.
26. H. Matthiesen, *A Novel Method to Determine Oxidation Rates of Heritage Materials in Vitro and in Situ*, in *Studies in Conservation*, 52, 2007, 271-280.