Preservation of the VASA Warship

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Published in:

2011

Citation for published version (APA):
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Introduction
VASA is a complete 17th century warship, the largest artifact of its kind in the world with a mass of ca 900 tons and with more than 20 000 loose wooden objects. So far she has attracted more than 30 million visitors (at present 1.2 million/year); thus being one of the major cultural heritage attractions in Scandinavia and Europe.
The ship sank in 1628 in Stockholm harbor during her maiden voyage. The wreck was relocated during the 1950s and was raised to the surface in 1961. The absence of shipworm in the brackish waters of the Baltic Sea and 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, mainly oak. Attacks by erosion and sulfur-metabolizing microorganisms softened 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. Large amounts of PEG and boron compounds were added to the timbers in this process. 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. This has been the subject of intense multidisciplinary research by an international group of scientists during recent ca 10 years.

Current state of knowledge
Microbial activity under the present dry conditions is negligible, but it has been important during the time on the seabed and probably also during the wet phases of the conservation; previously active microbial species have been identified by DNA and RNA analysis. Current wood degradation is caused by chemical processes, involving sulfur and iron compounds in combination with the humidity of the wood and atmospheric oxygen. The 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 were observed in the 90ties. By use of X-ray diffraction and synchrotron-based X-ray absorption near edge spectroscopy (XANES) the chemical composition of these deposits have been identified, and the mechanism of their formation is currently being studied in climate chamber experiments. Speciation and spatial distribution of sulfur and iron compounds in the timbers has been elucidated in detail by use of synchrotron-based methods, i.e. XANES and scanning X-ray microscopy (SXM), together with X-ray fluorescence, ESCA, scanning electron microscopy and X-ray powder diffraction. 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, however, sulfuric acid concentrations are negligible, and cellulose degradation as observed by means of size exclusion chromatography might be due to free radical reactions of Fenton type and/or acid hydrolysis caused by organic acids, in particular oxalic acid. Mechanical properties of VASA wood is studied by use of axial tension measurements and there is a positive correlation between the mechanical weakening and the extent of chemical degradation. The long-term changes of the wooden structure of the ship are monitored by use of a precise geodetic positional system. The changes are slow and most probably also not linear over time. Chemical degradation and mechanical weakening are important also in the deep interior of the timbers.

**Lacks of knowledge; demands on specified themes**

Still unknown key parameters are the exact nature of the various possible chemical degradation reactions, their individual rates and their relative contributions to the overall ageing of the wooden material. These basic data will affect the expected life-time of the whole ship. Attempts to determine the time dependence of the chemical processes by oxygen consumption measurements are not sufficiently conclusive due to the heterogeneity of the materials. 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 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 over 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.

**Forefront topics**

Methods for evaluation of the precise nature and rate of the chemical degradation processes have to be developed, and methods to stop or at least decelerate these processes under museum conditions must be given high priority. 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 oxygen. Environmental parameters such as relative humidity, temperature, light, and support structure have to be optimized. Hi-tech climate systems in museums are a necessity for successful preservation. Development of novel conservation and stabilization agents will also 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 such as iron. This is an important field for future research in organic synthesis and supramolecular chemistry.

The occurring chemical processes are inherently slow, and there is a big problem in determining their absolute rates, since accelerated ageing experiments and oxygen consumption measurements are difficult to interpret. An alternative would be to quench reactions for a long period of time (decades) by storage of specific samples under well-defined conditions at low temperature and inert gas for future analysis, comparing the result with wood aged under normal museum conditions.

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 complemented by systematic observations of the movements of the hull structure and with 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.

**New technologies**

Chemical analysis of archaeological wood, based on a wide spectrum of instrumental methods, has been successfully developed during the last 15 years and has resulted in 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, X-ray scattering and calorimetry. Technologies and facilities for long-term storage of quenched wood samples under low temperatures and inert gas should be developed, as well as technologies based on novel consolidants.

**Needs of interdisciplinary research**

Successful preservation work necessitates close co-operation between scientists and practitioners. Preservation technology has become increasingly more advanced and is now based on front-line research. A successful knowledge transfer from scientists to practitioners will most certainly in the future necessitate increased recruitment of scientifically trained museum staff.

Conservation is by nature interdisciplinary. For VASA, close co-operation between specialists in wood chemistry and technology, molecular biology, physical, inorganic and organic chemistry, materials science, nanotechnology, mechanical engineering, computer science and conservation science will be of future increased importance.
Acknowledgement

The Swedish National Maritime Museums’ research programs “Preserve the Vasa” and “A Future for Vasa” are/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.