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The sulphur threat to the 17th century warship Vasa

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Abstract

The royal warship Vasa sank on her maiden voyage in 1628. She was discovered in 1956 and in 1961, after 333 years at the bottom of the sea in the Stockholm harbour she was salvaged. Vasa, built mainly of oak, was one of the first major objects to be conserved with polyethylene glycol. She was sprayed continuously for 17 years followed by an 11 year long controlled drying procedure (Håfors, [1]). In 1990 the new Vasa museum opened and is now the most visited museum in Scandinavia with about 750 000 visitors each year.

The summer of 2000 was unusually wet and in July, yellow-white precipitate was discovered on wooden surfaces on objects kept in the storage, in showcases and later on the ship itself. An international seminar was held in February 2001 and as a result a research programme was launched that involves scientists from Australia, Canada and Sweden.

Surface as well as core samples have been analysed in this research programme by a range of chemical methods. The results so far show the presence of elemental sulphur in the outermost layers of the ship. This sulphur is now being oxidised in the museum environment to sulphuric acid. The process is probably catalysed by iron ions. Subsequently acid hydrolysis of the cellulose threatens the stability of the wood. Up until now about 1200 areas with precipitates have been observed on the ship and about 400 loose finds are affected.

Treatments to neutralise the acid are currently being carried out and will be presented as well as experiments to extract the iron using strong chelating agents.



1 Introduction

The conservation of *Vasa* using polyethylene glycol (PEG) $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ started in 1962 and finished 17 years later in 1979. Initially the molecular weight 1500 in an aqueous solution was used but in 1971 it was changed to PEG 600 as research showed that the lower molecular weight had a greater dimensional stabilizing effect on the wood. The conservation started with spraying a 10% solution which was gradually increased up to 45%. A fungicide was added to the solution, borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and boric acid (H_3BO_3) in the ration 3:7, about 4%. The PEG concentration was raised when equilibrium was established between the PEG concentration in the solution and the PEG in the wood. After the spraying had stopped in 1979 *Vasa* was slowly dried in a controlled atmosphere. The hull was surface treated with a 45% solution of PEG during 1981 to 1988, molecular weight 4000. In 1988 she was towed on her pontoon into the purposely-built museum (Håfors, [1]).

The *Vasa* Museum is built as one large hall where the ship is displayed in the centre with the exhibitions surrounding it. A climate control system was installed in 1988 and the climate was set at 17°C and 57% relative humidity (RH) in the winter and 20°C and 60% in the summer (Håfors, [1]). The climatic variation between summer and winter depended on constructional aspects in the building but it corresponded to a moisture content in the wood of about 12%. Ever since the museum opened the climatic system has failed during warm and humid summers. The RH levels have increased well over 60% and sometimes over 70% in the storage area. The summer of 2000 was unusually rainy and as a result the museum was crowded with visitors wearing wet clothes and umbrellas.

2 Research project

About 6 months after the discovery of the precipitates, the museum in February 2001 arranged an international seminar, including conservators and scientists from Australia, Denmark and Sweden. The viking ships in Roskilde, Denmark and the *Batavia*, from 1629, in Western Australia has earlier experienced similar problems. These precipitates were thought to be an effect of the formation of iron sulphides (pyrite) in the oak wood and also directly related to high humidity levels (Jespersen, [2]). As a result of the seminar a research project was launched which includes the Universities of Stockholm and Uppsala, the Swedish University of Agricultural Science in Uppsala, the University of Calgary, Canada and the Western Australia Maritime Museum (Sandström et al., [3], [4]).

The aim of the project, which is called *Bota Vasa* (Cure the *Vasa*), is: To develop analytical methods for identifying sulphur and sulphur oxidation. To investigate possible bacterial activity and the effect of iron compounds as a catalyst on the sulphur oxidation process as well as the reaction speed. To find a suitable method for extracting iron as well as sulphur from the wood (Sandström, [3]). The project also investigates the long-term stability of the polyethylene glycol and how it interacts with iron ions. This is of great interest as PEG is widely used as a conservation liquid. Comparative analysis will be executed on

other wooden finds both submerged and conserved and the aim is to find a treatment that can be used on marine archaeological objects.

2.1 Analytical methods and results

The initial analysis was done with X-ray powder diffraction (XRD) on surface samples and it showed various crystalline hydrated sulphate salts, gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and also the iron sulphates natrojarosite, $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, and melanterite, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$. In some places crystals of elemental α sulphur S_8 were identified (Sandström et al., [3]).

The sulphur in core and surface samples was analysed by X-ray absorption spectroscopy (XANES) at the Stanford Synchrotron Radiation Laboratory, California, USA, and used for the first time to characterise sulphur compounds in wood (Sandström et al., [3]). The spectra of the core samples show that elemental sulphur is the dominating form and furthermore, the spectra indicate different stages of oxidation along the length of the core, with elemental sulphur deep in the samples and oxidised sulphur intermediates closer to the surface. Analyses of total sulphur show that the concentration varies between 0.2 and 22 mass percent in the outermost layers of the wood (Sandström et al., [4]).

The third method that has been used is X-ray photoelectron spectroscopy (XPS), at the University of Uppsala, Sweden (Sandström et al., [3], [4]). The method is used to map the distribution of all elements except hydrogen in the samples. Sulphur was detected as well as boron, residue from the added fungicide that had penetrated the whole of the core. Iron, from rusting bolts, has also penetrated deep into the wooden structure.

2.1.1 Core sampling

13 core samples from various levels inside the Vasa ship have been analysed. (fig. 1) (Sandström et al., [4]). About half of the samples are from unaffected areas. All cores contain sulphur, particularly in the surface layers but the amounts vary considerably. It seems that the lower part of the ship that was covered with clay and silt during the time submerged is generally in better

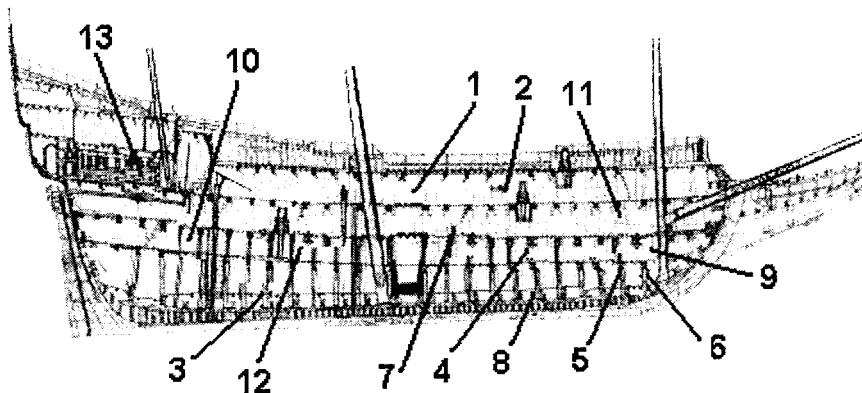


Figure 1. 13 core samples were taken from various locations on the ship [4].

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condition than the wood on higher levels that was exposed to seawater. It seems that the clay prevented water to penetrate wood and thus the accumulation of sulphur. This could also indicate that this type of decay would be more common on marine finds than on archaeological remains found on land.

2.1.1.1 The Sulphur problem The sulphur originates from sulphate ions in the seawater. At the time when the Vasa was submerged the unrestricted waste dumping from the growing city made the waters of the Stockholm harbour increasingly polluted. Sulphate reducing bacteria are able to use sulphate instead of oxygen when decomposing organic matter under anaerobic conditions. Around the Vasa this organic matter created an almost completely oxygen free environment. As a source of oxygen, the bacteria reduced the sulphate ions in the seawater to hydrogen sulphide. When the water penetrated the wood it brought along the H₂S, which was transformed and stored as elemental sulphur, the stable sulphur form in anaerobic environment. The presence of between 0.2% and 6% sulphur have been detected in the surface layers of the Vasa wood. (fig. 2.) The oxidation process of elemental sulphur can damage the wood in different ways. The volume expansion of the wood can cause mechanical damage but a more serious problem is the production of sulphuric acid.

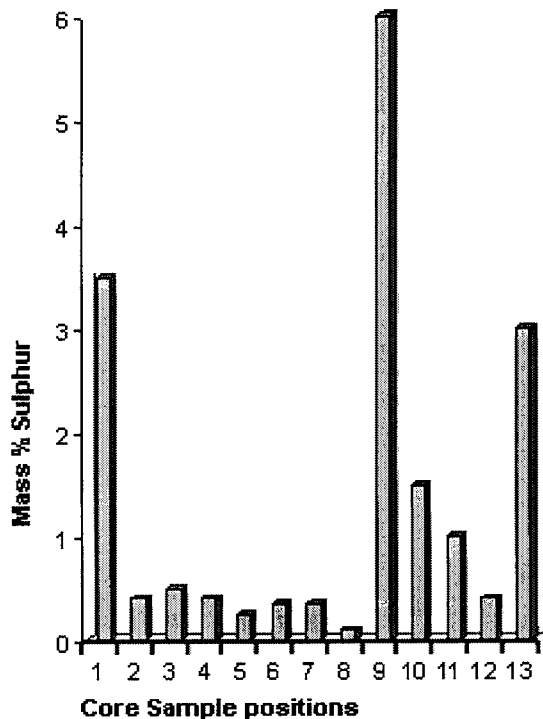


Figure 2. The figure shows the amount of sulphur in the outermost layers of the wood (Sandström et al., [4]).

The low pH values and sulphate salts on the moist timbers show that sulphuric acid has been produced (Sandström et al., [4]). The pH, measured with wide-range pH-paper show pH values between 1 and 3.5. The wood itself is slightly acidic and has a pH of about 5. The oxidation of elemental sulphur requires water and oxygen and the resulting low pH is known to damage wood by acid hydrolysis (Sandström et al., [4]).

The reaction needs a catalyst to proceed with significant speed. There are indications that the oxidation process might be promoted by iron (III) ions. The iron ions come mainly from the original iron bolts, about 5000 that rusted away in the seawater. During and after the salvation of Vasa new iron bolts were inserted. These were coated with epoxy and/or zinc and after 40 years some show signs of corrosion. Possibly, the PEG interact with the iron ions and promote corrosion of the metal. The oxidation process is thus constantly fed with new catalyst. Another possibility that is currently being looked into is if also bacteria can act as a catalyst, by itself or in conjunction with the iron. On the other hand, the boric acid used in the conservation process as a fungicide could limit bacterial activity.

3 Treatment

3.1 Temporary treatment

Currently, long-time financial support, at least four years, is sought to carry on the research project. The aim is to find a suitable treatment to remove the sulphur and the iron compounds. Meanwhile the visibly affected areas are being neutralised with a 5% bicarbonate buffer mix: 7 parts of NaHCO_3 and 1 part of Na_2CO_3 at a pH of about 9,5. On horizontal areas the liquid is applied with thick absorbing cloth and covered by plastic sheets to prevent the mixture from drying too quickly. The treatment raises the pH to about 6 and the harmless products carbon dioxide CO_2 and sodium sulphate Na_2SO_4 (aq.) are formed. On vertical areas the liquid is sprayed on and then covered with plastic. Here two treatments are normally needed to raise the pH to a sufficient level. To follow up the rate of the sulphur oxidation the pH was measured regularly in 68 places. The first treatment was done in Nov/Dec 2001 and it took about two months to complete and the summer 2002 the second treatment was conducted. Monitoring of the affected areas show that the pH is slowly decreasing down to harmful levels. Naturally the treatment using thick absorbing cloth is more effective.

3.2 Iron removal

Because of the possibly catalysing effect of the iron on the sulphur oxidation, it is essential to remove the iron from the wood. This can be achieved by using a chelating agent that forms strong soluble complexes with iron (III) ions (Sandström et al., [4]). EDTA is widely used among archaeological conservators but experiments are done with a derivate that creates stronger complexes with Fe (III) ions. We have named it EDMA ethylenediiminobis (2-hydroxy-4-metyl-



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phenyl) acetic acid and is commercially used in large quantities as an iron micro-nutrient for citrus agriculture in the Mediterranean and South East Asia (Sandström et al., [4]). It is purposely made by a Swedish company for the Vasa project without the iron added to the complex. The EDMA has one disadvantage and that is the very dark red colour of the iron complexes. Therefore, parallel tests are also being conducted with another complex called DPTA (diethylenetriaminepentaacetic acid) that is light yellow but maybe not quite as effective as the EDMA (Sandström et al., [4]). We are beginning to experiment with tank treatment on smaller objects but for bigger objects we have to use spraying techniques or use rugs. The EDMA and DPTA will be used together with the bicarbonate mixture. The long term stability of the complexes must of course be studied before we do any large-scale treatment.

4 Conclusion and the long term preservation of the Vasa ship

A combination of analytical methods reveal that large amounts of elemental sulphur has accumulated in the surface layers of the Vasa wood while the ship was submerged under low oxygen conditions (Sandström et al., [3], [4]). This sulphur is now being oxidised in the museum atmosphere to sulphuric acid. The estimated amount is about 2000 kg of elemental sulphur that can form sulphuric acid. So far we have neutralised about 10 kg of acid. The Vasa ship is facing severe problems in the future. It is vital for the long term stability of the ship that we find a solution to this problem. The aim of the Vasa project is to find a Vasa “cocktail” that can both efficiently neutralise the sulphuric acid and at the same create complexes with the iron ions. The Vasa ship is a very complex structure and so far we can only treat the visible and easily accessible areas. A great problem is the many hidden areas of the ship and more efficient application techniques have to be worked out. Closely related to this is the climate in the museum. Presently the system is being rebuilt and enlarged. If research establishes that iron catalyses the oxidation of sulphur to sulphuric acid some or all of the new inserted iron bolts have to be replaced. The ship is lying in a stainless steel cradle and it has to be rebuilt in order to better support a weakened structure.

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