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DEGRADATION OF ARCHAEOLOGICAL TIMBERS BY PYRITE: OXIDATION OF IRON AND SULPHUR SPECIES.

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SUMMARY

The timbers recovered from the wreck of the *Batavia* (1629) have been conserved in a batch-wise process by impregnation with aqueous solutions of polyethylene glycol (PEG), which was followed by controlled dehumidification.^{1,2} The treatment programme was effected over a period of ten years owing to the limited impregnation facilities and the need for extended periods of drying.³ During the erection of the supporting steel structure it was noticed that several of the timbers that had been in the first treatment batches were friable and very acidic. Identification of the minerals amongst the fibres showed up the presence of a wide range of iron and sulphur containing species. This paper reports on the origin of the iron sulphides and the first stages in the amelioration of the acidity resulting from the oxidation of pyrite. These problems manifested themselves several years after completion of the PEG impregnation treatment.

INTRODUCTION

The Dutch East Indiaman *Batavia* (1629) was wrecked on Morning Reef in the Houtman Abrolhos and the remains lay undisturbed until excavations began in 1970. Owing to the exposed nature and shallow depth of the site the surviving timbers were excavated and recovered piece by piece.⁴ This procedure facilitated the conservation programme and enabled them to be treated in a batch-wise process. An inspection of the site plan (see Fig. 1) showed that the timbers had been covered by a series of iron cannon which, together with several thousand cannon balls from the shot room, provided the source of iron contamination. The encapsulating marine concretion created an essentially anaerobic micro-environment⁵ in which the iron cannon and shot corroded to an extent that was dependent on the proximity of bronze cannon (see Fig. 1), the water depth and the water movement across the site.⁶ As the primary iron corrosion products diffused into the oak wood the activity of sulphate reducing bacteria would have resulted in relatively high concentrations of sulphide ions and subsequent precipitation of the iron sulphide pyrite, FeS₂. Measurements of on-site corrosion potentials and surface pH of concreted iron objects gave a range of values with Eh -0.30 ± 0.12 and a mean pH of 4.8 ± 0.5 ⁶. Inspection of the relevant Pourbaix diagrams shows that under the above range of conditions pyrite is the thermodynamically stable form of iron and sulphur⁷. Pyrrhotite is also formed under the upper range of Eh conditions.

A representative sample of heavily degraded timber was ashed at 500° C in an electric furnace and the resultant mineral content amounted to 30.5 wt%. This shows that major problems exist with regard to the inherent stability of the timbers. Since pyrite has a molar volume of 24 cm³ and the commonly found oxidation product FeSO₄.4H₂O occupies

approximately 98 cm³, the four fold expansion results in great physical damage to the timbers. Since ferric ions are known to catalyse the degradation of cellulose⁸ and the acid produced from the oxidation of pyrite also promotes hydrolysis, it is essential to find solutions to these combined problems. If left unchecked the timbers would disintegrate and this unique historical record of early 17th century Dutch shipbuilding would be lost.

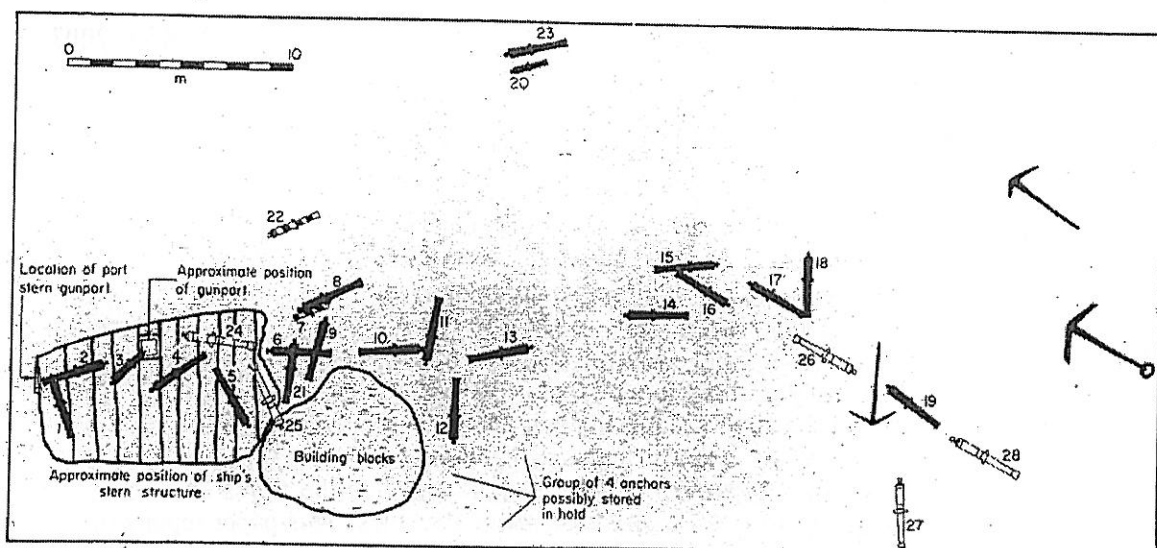
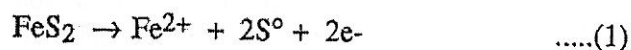


Fig. 1: Site plan of the *Batavia* wreck. The black cannons are made of iron and those in outline are bronze⁴.

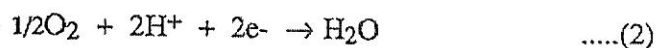
OXIDATION OF PYRITE

The oxidation of the iron sulphide pyrite (FeS₂) has been the subject of extensive research since it has major economic implications in the mining industry.⁹ Reports of very rapid oxidation resulting in the loss of museum mineral specimens¹⁰ and the effects of ferrous sulphate tetrahydrate on PEG conserved archaeological timbers have recently been reported.¹¹ It is important to understand that the oxidation process can occur through two routes, one microbiological and the other thermodynamic. Both these processes are very dependent on the relative humidity (RH). In fact Berzelius first reported the effects of RH on pyrite oxidation in 1819. For microbial oxidation by bacteria, such as *thiobacillus ferrooxidans*, the rate of reaction increases most dramatically once the RH exceeds the value of 60%.¹²

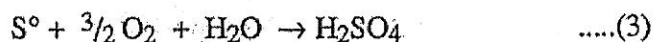
The conversion of pyrite to ferrous sulphate involves the initial anodic reaction,



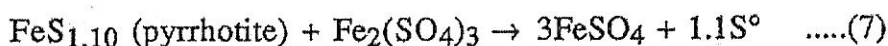
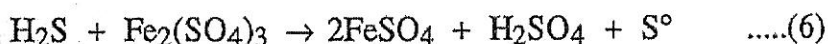
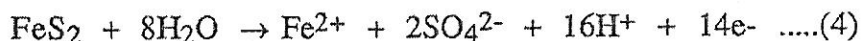
while the cathodic reaction is reduction of oxygen, viz.



which can be subsequently followed by bacterial oxidation of elemental sulphur to sulphate as

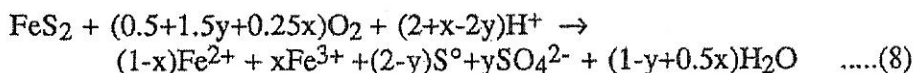


Although it is voluminous the elemental sulphur formed does not inhibit the oxidation of pyrite since the rate determining step is oxygen diffusion and acceptance of electrons. The overall reaction scheme is very complex¹³ and involves the reactions listed above as well as



It can be seen that once iron (III) sulphate has been formed (equation 5) it can act as an oxidizing agent to convert any hydrogen sulphide or pyrrhotite to ferrous sulphate and elemental sulphur (equations 6 and 7). A sulphur rich iron sulphide was also found on the surface of the timber near the pyrite crystals whose composition was consistent with the more reactive iron sulphide pyrrhotite (see equation 7). The presence of elemental sulphur was confirmed by extracting the surface material with carbon disulphide. The resultant yellow solution yielded orthorhombic sulphur on evaporation of the solvent.

It is possible to write an overall reaction scheme for the oxidation of pyrite as follows;



Experiments with isotopically pure $^{18}O_2$ and H_2O ¹⁶ indicate that the initial oxidation is by molecular oxygen until significant amounts of ferric ions are produced. The Fe(III) ions then act as the principal oxidising agent responsible for the oxidation of pyrite.¹⁴

To confirm that the white crystals found on the surface of the affected timbers was due to pyrite oxidation products, surface material was examined by X-Ray Diffraction and the iron-sulphur species were identified. SEM inspection and EDAX analysis of the crumbling timber samples showed up the presence of etched pyrite crystals and considerable amounts of elemental sulphur. The species identified are listed in Table I.

Table I: Materials identified by X-Ray Diffraction on degraded *Batavia* oak wood.

Name	Chemical Formula	Index No.
Goethite	$\alpha\text{FeO}\cdot\text{OH}$	17-536
Lepidocrocite	$\text{FeO}\cdot\text{OH}$	8-98
Iron(II) hydroxide	$\text{Fe}(\text{OH})_2$	13-89
Orthorhombic sulphur	S	8-247
Pyrite	FeS_2	26-801
Rozenite	$\text{FeSO}_4\cdot 4\text{H}_2\text{O}$	16-699
Siderotil	$\text{FeSO}_4\cdot 5\text{H}_2\text{O}$	22-357
Natrojarosite	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$	11-302
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	22-827
Bilinite	$\text{Fe}_3(\text{SO}_4)_4\cdot 22\text{H}_2\text{O}$	25-1153
Butlerite	$\text{FeSO}_4(\text{OH})\cdot 2\text{H}_2\text{O}$	23-304
Roemerite	$\text{FeFe}_2(\text{SO}_4)_4\cdot 14\text{H}_2\text{O}$	13-530

There were no indications of halite (NaCl) and the major white sparkling material was identified as the tetrahydrated iron (II) sulphate, rozenite. The absence of 'salts' derived from sea water is consistent with the long period of desalination (two years) and the long periods of impregnation (2-3 years). The presence of both jarosite and natrojarosite indicates that despite several years immersion in treatment tanks there is a sufficient concentration of both Na and K to allow these compounds to form. However it should be noted that both these minerals are commonly observed oxidation products of pyrite and that they tend to act as natural chemical buffers¹³. The presence of elemental sulphur and so many iron (II) and iron (III) sulphates was proof that oxidation of pyrite had occurred. The worst affected timbers were those which had previously been stored for several years at a nominal 60% RH. Owing to shake down problems with the building and the corroded and dilapidated dehumidifiers the relative humidity had often reached levels as high as 70% before returning to a free air space value of 60% RH. One of the problems is that the pyrite crystals are in the cells of the PEG impregnated wood which may have had an effectively higher relative humidity owing to the inherent hygroscopicity of the PEG 1500 and the nature of the degraded timber itself. The relative humidity of the storage environment has been reduced to 55%RH. since the nature of the problem was identified.

TIMBER ACIDITY

Apart from having a 'sharp' smell the badly affected timbers had a white to yellow colour and the surface pH of the wood was far from being neutral (see Fig. 2 and Table II). The visual appearance of the timbers correlated closely with the surface pH, viz. those which were dark grey had near neutral pH while the mineralised yellow surface planks had pH values as low as 1.2. The results of more than one hundred measurements are summarised in Table II.

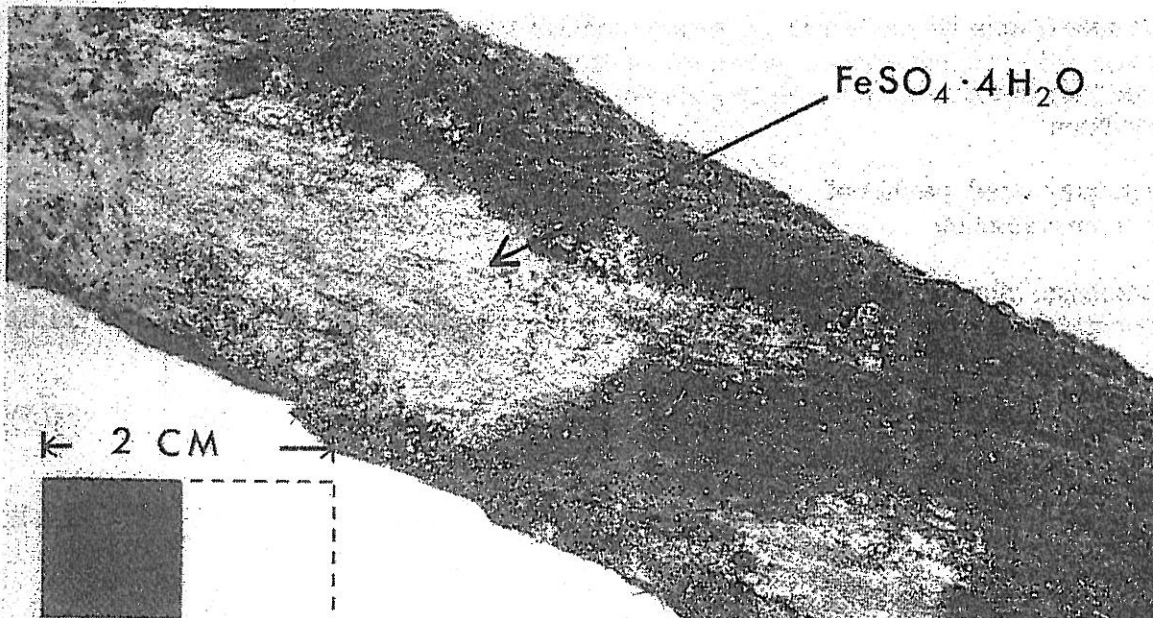


Fig. 2: A heavily degraded section of *Batavia* timber showing extensive mineralisation. Photo: Jon Carpenter.

The pH of the PEG 1500 solutions in the impregnation tanks was checked and with values of 7.2 for 60 wt% and 90 wt% concentrations in two of the tanks in use, the surface acidity cannot be due to the PEG 1500 itself. The natural acidity of saturated solutions of ferric sulphates and hydroxy oxides was found to span the range between pH 2 and pH 3. Hydrolysis of iron (III) species will also contribute to the timber acidity. The iron sulphates found on the surface of the timbers (see Table I) can clearly give rise to acidity in this pH range. The lower pH values observed on the (extremely degraded) timber samples is most probably due to the sulphuric acid derived from the oxidation of pyrite as shown in equations 4 and 6. The acidity due to oxidation of pyrite as described by the overall equation (8) reaches a maximum at pH 1.0 in 0.17M H₂SO₄.¹³ It became immediately apparent that some process had to be developed to reduce the acidity of the timbers and halt the oxidation and acid hydrolysis of the cellulose. The preferred method needed to be non aqueous since we did not have the fiscal resources to immerse the timbers in a water-based deacidification system, reimpregnate with PEG and once more dry them out through the process of controlled dehumidification.

Table II: Surface pH and general description of *Batavia* timbers.

General Description	pH Measurements		
	Range	Average	(S.D.)
dark grey with waxy PEG 1500 surface	7↔9	7.8	(±0.7)
dark waxy	5.4↔6.8	6.1	(±0.5)
extensive regions of Fe (III) corrosion products	4.5↔4.8	4.6	(±0.1)
light grey timber, poor condition	2.5↔5.0	4.1	(±0.9)
light grey wood, patches of rich mineralisation	2.0↔3.5	2.7	(±0.5)
yellowish, mineralised regions extremely poor condition	1.7↔4.4	2.8	(±1.0)
light wood, extensive mineralisation, poor condition	1.2↔3.2	2.2	(±0.7)
extreme degradation, very rich mineralisation	1.3↔2.3	1.7	(±0.4)

MICROBIOLOGICAL ASSAY

In order to clarify the mechanism leading to the development of such high surface acidity it was decided to take sterile swabs of the timber and see if any micro-organisms could be identified. It is well known that bacteria such as *thiobacillus ferrooxidans* are responsible for the leaching of pyritic mineral deposits and for the production of sulphuric acid which destroys reinforced concrete sewer system.¹⁵ Only one inoculation of the culture medium produced evidence of thiobacilli. This type of micro-organism is, however, notoriously difficult to grow and so the absence of specific identification of the microflora does not preclude their involvement in the process. It was interesting to note that the timbers have very low levels of "normal" bacteria and are essentially sterile. The results indicate that the major component of pyrite oxidation appears to be under chemical and not microbiological control.

DEACIDIFICATION

Five non aqueous methods of deacidification were investigated along with one water-based trial. Attempts to deacidify the surface with a 3 wt% solution of methylmagnesium carbonate spray had minimal effect since the mean surface pH changed from 2.4 ± 0.3 before treatment to 2.8 ± 0.2 after treatment. Attempts to neutralize the surface with a 2 wt% urea solution in methylated spirits were largely ineffective since one week after

treatment the mean surface pH was 3.1 ± 0.3 compared with an initial value of 2.7 ± 0.5 . Similarly the use of a 0.05M sodium hydroxide solution in methylated spirits proved to be of no use whatsoever.

Two amine-based treatments proved to be effective. Both versions of the ammonia treatment (gaseous ammonia and saturated ammonia solution) and straight diaminoethane were effective in changing the surface pH of the trial samples. The acidity fell dramatically after initial treatment which involved either exposure to ammonia vapour or direct 'spraying' of the surface with the solution. The pH gradually fell with reaction time until it plateaued after 22 ± 2 days for the aqueous concentrated ammonia treatment whilst the ethylenediamine treatment did not reach a plateau level for several months. The rate of change of surface pH with time is shown in Fig. 3 where the pH of the timber is plotted as a function of the logarithm of the elapsed time (in days) since the initial spraying.

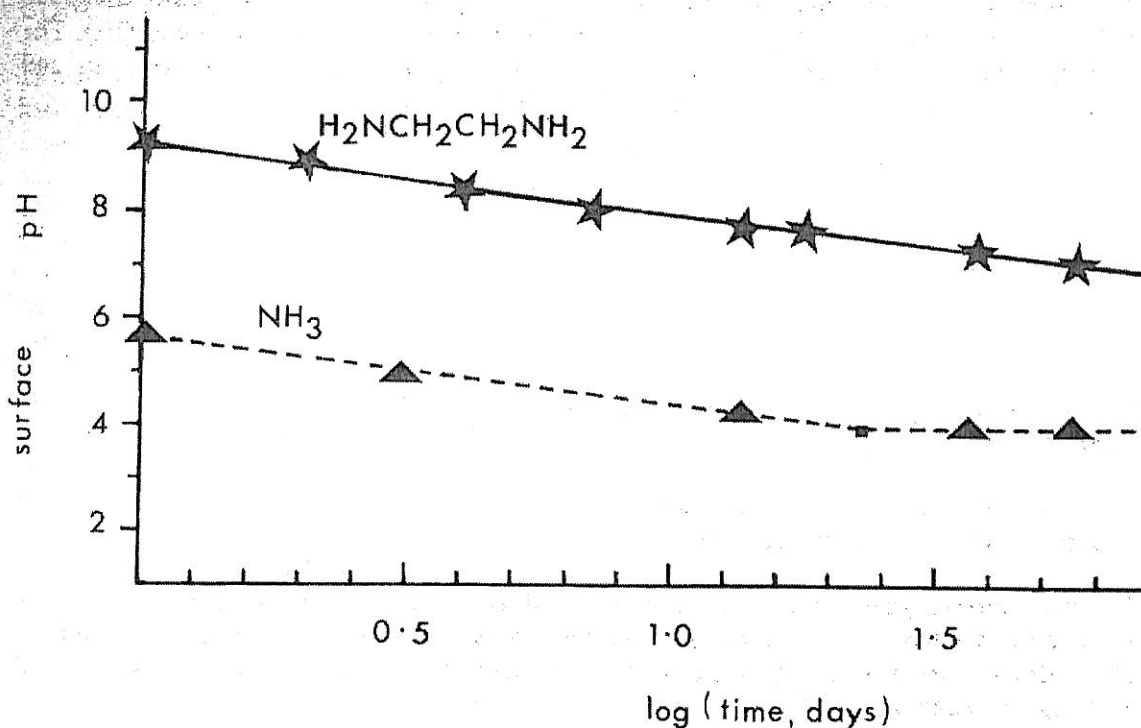


Fig. 3: Plot of surface pH versus logarithm of time after deacidification for amine based treatments.

Both the ammonia and ethylenediamine treatments followed the equation:

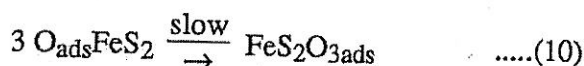
$$\text{Surface pH} = C - k \log T \quad \dots(9)$$

where C and k are constants and T is the elapsed time in days after the initial treatment. The C values were 9.23 and 5.62 for ethylenediamine and ammonia with their respective 'slope' or k values of 1.24 and 1.21. The different C values reflect more the lower volatility of ethylenediamine (BP. 116.5°C) compared with ammonia (BP. -33.41°C). The scatter of data points is such that the constants are within experimental error of each other since

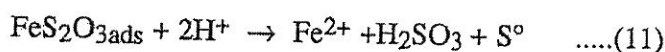
the variance in the slope is ± 0.3 . The logarithmic dependence of the pH is indicative of a chemically controlled phenomenon rather than being simply due to the outward diffusion of the amine and the same slopes indicate that the rate is being controlled by the same phenomena. The plateau value of the pH from the ammonia treatment was 4.0 which is indicative of the equilibrium values expected for the iron (III) corrosion products on the surface.

Given the high toxicity of ethylenediamine (TLV 10ppm compared with ammonia at 25ppm) it was decided to bulk treat the worst affected timbers with gaseous ammonia at a local pest control facility since the 200kg of timber could be treated under a gas-proof membrane. The surface colour changed to the characteristic red brown of iron hydroxy oxides and a total of 2.85kg or 1.7 wt% of neutralized oxidation products were removed by dry blasting. The species additional to those in Table I are listed in Table III.

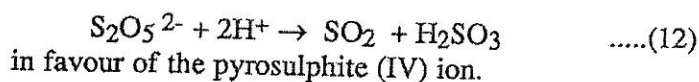
The species identified on the surface of the timbers after the ammonia treatment included an ammonium pyrosulphite, $(\text{NH}_4)_2\text{S}_2\text{O}_5$, with sulphur having the formal oxidation state of IV, i.e. an intermediate step in the oxidation of elemental sulphur to sulphate (VI). The chemical oxidation of pyrite in aqueous solution involves adsorption of oxygen and subsequent oxidation to an intermediate thiosulphate species viz.,



Thiosulphate then desorbs and disproportionates viz.,



In a similar way the presence of the sulphur(IV) species $\text{S}_2\text{O}_5^{2-}$ which was isolated as the ammonium salt from the timbers is probably due to ammonia shifting the equilibrium



This may indicate that the conversion of pyrite through to iron (III) sulphates takes place via a series of two-electron steps. The presence of a wide range of hydrated ammonium iron sulphates is not unexpected since the ammonia essentially acted as an acid neutralizing reagent.

Table III: Species identified by XRD on ammonia treated timber.

Name	Formula	Index No.
Mohrite	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	17-481
Ammonium iron(II) sulphate hydrate	$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	18-107
Ammonium iron(III) sulphate	$(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$	3-43
Ammonium pyrosulphite	$(\text{NH}_4)_2\text{S}_2\text{O}_5$	24-12

Table III (continued)

Name	Formula	Index No.
Ferrinatrite	$\text{Na}_2\text{Fe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	22-1382
Potassium iron(II) sulphate hydrate	$\text{K}_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	17-486
Iron oxide sulphate hydroxide(green rust)	$\text{Fe}_{3.6}\text{Fe}_{0.9}(\text{O},\text{OH},\text{SO}_4)_9$	13-90
Iron sulphate hydroxide	$2\text{Fe}(\text{OH})\text{SO}_4$	21-428
Iron sulphate hydroxide	$\text{Fe}_4(\text{OH})_{10}\text{SO}_4$	21-429

CONCLUSION

The acid-affected oak timbers from the *Batavia* appear to be mainly confined to those that had previously been stored after treatment at an RH above 60%. These first batches of timber had also suffered from immersion in a tank of PEG 1500 that had been oxidized by bacteria and moulds during a plant breakdown. The putrid PEG was drained and a new solution used to complete the treatment. The prolonged immersion for several weeks in the putrid solution may have activated the pyrite in the timber and made it more prone to oxidation. Three years after the ammonia treatment the surface pH of the acid-affected oak wood remains around a pH of 4. Since the mechanism for continuing oxidation of pyrite involves the ferric ion, the effective removal of labile Fe (III) species by ammonia does much to enhance the stability of the timbers.¹⁴ The consolidation of the highly degraded timber has been investigated by Vicki Richards and is the subject of a coming report.¹⁶ The most important point to remember is to treat all wood from shipwrecks as being inherently contaminated with iron sulphides such as pyrite and to take appropriate precautionary measures in the control of relative humidity during storage and display.

ACKNOWLEDGEMENTS

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