

# Analytical report on corroded nails from *Peggy*



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by David Watkinson, Cardiff University.**

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# PEGGY: ANALYSIS OF NAILS AND WOOD

## 1. Background and context for analysis

### 1.1 Samples and instruction

Samples from 6 nails and surrounding wood used to construct the wooden boat Peggy were submitted for analysis to David Watkinson at Cardiff University. Permission was granted for destructive sampling to provide underpinning knowledge necessary to develop conservation rationale for Peggy. The nails were received labelled as in table 1.

Labelling of nail	Composition
0014/1	Iron and wood core
0014/2	Iron and wood core
0014/3	Iron and wood core
0014/4	Iron and wood core
0014/5	Iron and wood core
0014/6	Iron

Table 1 - Nail sample numbers from Peggy's hull.

### 1.2 Corrosion context

Corrosion in the atmosphere requires oxygen, moisture salts dissolved in the moisture to form an electrolyte. If one of these variables is completely removed corrosion will cease. By way of introduction to the analysis some background corrosion is discussed.

#### 1.2.1 The schooner *Peggy*

The *Peggy* spent much of her life within a marine environment, where the sea provides a good electrolyte for corrosion of metals (Trethewey and Chamberlain 1988). This is illustrated by the use of seawater to construct the *galvanic series*, which measures the corrosion potential of metals and alloys in seawater against a reference electrode (Jones 1992:170). Within the galvanic series low alloy steel has a low corrosion potential. All the nails from *Peggy* will be examined to determine the nature of their corrosion.

Once *Peggy* was removed from seawater corrosion is not expected to have ceased. The absorbent wooden hull of the ship will contain chloride bearing hygroscopic soluble salts from seawater and soluble corrosion products from metal corrosion. They will attract water in relation to the prevailing moisture content of the atmosphere (relative humidity). This will make the wood damp and offer an electrolyte in contact with the nails driven into it.

Some salts from marine contexts and corrosion products of iron cause iron to corrode at very low relative humidity (Spencer 1926, Richardson and Malthus 1955, Evans and Taylor 1974, Chandler 1966, Watkinson and Lewis 2005b). This creates a conflict of interest in storage conditions for metals and wood. Dry storage will reduce metal corrosion, but will cause wood to lose moisture integral to its structure and it will shrink as it equilibrates with its dry environment. Structurally ships were made to sit in water where the wood is hydrated and swollen by moisture. Paint layers may reduce rate of moisture loss from wood once it is out of the water, but micro cracks and discontinuities in the coating will mean that moisture loss cannot be prevented. The equilibrium moisture content of the wood will relate to the ambient environment and its rate of change. Metals driven into salt infested wood will remain at risk from electrolytic corrosion as: there will be salt residues from the marine environment in the wood and the ambient environment provides water to hydrate the wood and dissolve the salts it contains to support electrolytic corrosion.

### **1.2.2 Iron Corrosion**

Iron and its alloys are particularly at risk from corrosion, both in the seawater and following removal into the atmosphere. This result is from the nature of the corrosion process it undergoes in chloride infested environments. It is normally expected to form a range of ferric oxyhydroxides (FeOOH) and may also form magnetite (Fe<sub>3</sub>O<sub>4</sub>), where oxygen levels are low in sediments or deep within the wood (Gilberg and Seeley 1981, Turgosse 1982a). In estuarine conditions and sediments low in oxygen, but rich in sulphate reducing bacteria, iron sulphides may form and their oxidation following excavation presents acidity problems (Fell and Williams 2004).

Once removed from the seawater corrosion does not cease, particularly for iron and its alloys. Ferric oxyhydroxides (FeOOH) can occur in four different crystalline forms known as alpha (α), beta (β), gamma (γ) and delta (δ). These are known as polymorphs, which are minerals that share the same chemistry, but have different crystal structures. The βFeOOH polymorph forms only in the presence of halide ions like chloride, which it incorporates into its structure and adsorbs onto its surface (Millikan 1965). It has been recorded on archaeological objects (Zucci et al 1977, Turgosse 1982b) and on marine iron (Watkinson and Lewis 2004). It actively corrodes iron in contact with it due to the aqueous mobility of its surface adsorbed chloride (Turgosse 1982b, Watkinson and Lewis 2004, 2005a and 2005b). Moisture for this corrosion mechanism can be provided by ambient relative humidity and tests reveal that it can corrode iron in contact with it at 15% relative humidity, with significant increases in corrosion rate above 20% relative humidity (Watkinson and Lewis 2004 and 2005a).

Corrosion of iron results in hydrolysis of ferrous (Fe<sup>2+</sup>) ions produced by corrosion of iron, which produces acid (Turgosse 1982b, Jones 1992, Selwyn et al 1999). This can hydrolyse the wood cellulose directly next to the corroding nail, leaving it weakened, acidified and heavily stained with

iron oxide. It can also infuse the wood with iron corrosion products that mineralise the wood in the vicinity of the nail, making it brittle and likely more hygroscopic. In conjunction with the total loss of the nail to corrosion this will lead to failure of physical integrity, which potentially places the entire ship at risk. There will be little visual evidence of this on the surface of the wood.

Low humidity can be employed to stop or reduce the rate of iron corroding, according to the level to which the humidity is lowered. This iron corrosion model raises problems for storage of organic material associated with it. Besides the capital and running costs required to attain the low humidity to prevent iron from corroding, any wood in contact with it will be incompatible with the recommended 20% relative humidity maximum allowable (Watkinson and Lewis 2004). By carrying out analysis that offers understanding of the metal corrosion processes an informed conservation design can be constructed.

## **2. Analysis Programme**

Taking into consideration the above information an analysis programme was designed to determine the corrosion processes occurring, which were then related to their current and future effects on the wood. This clarifies the conservation options available.

- Record and discuss the visual appearance of the nails (macro and micro photography) and assess.
  - Degree of corrosion of nails.
  - Extent of mineralisation of the nails.
  - Evidence for active corrosion of iron.
  - Mineralisation of the wood.
- Assess the pH of the wood infused with iron corrosion products.
- Determine the presence and quantity of chloride in the wood.
- Measure the chloride content of the iron.

## **3. Visual inspection of nails and wood**

### **3.1 Stability of the nails**

Visual inspection used a stereo microscope at magnifications of x4 to x 20 with digital imaging camera and software attached. The appearance of all iron nails followed a standard pattern (figures 1 and 3-8). Corrosion is seen soft orange-red-brown powdery, with a denser underlying corrosion layer that is darker. The upper layer is likely the interface between mineralised iron and residual iron core. Darker brown patches of soft corrosion and the hard surface of corrosion pustules will contain some  $\beta\text{FeOOH}$ . This is unstable and supports corrosion of iron at low humidity (Watkinson and Lewis 2005). Other lighter orange areas are likely to comprise mostly  $\alpha\text{FeOOH}$ , which poses no threat to the object.



Figure 1 – Sample 0014/: soft powdery corrosion on nail surface.

All the iron examined from the Peggy is highly unstable in damp atmospheres. This is evidenced by the range of corrosion pustules seen on the nails (figures 3-7). These are indicative of highly unstable iron and parallel pustules formation described by other researchers studying chloride infested iron (Turgoose 1982b, Knight 1990, Selwyn et al 1999).

Pustules are created by activation of electrolyte spots that are formed in high humidity. The electrolyte is supplied by soluble compounds on the metal surface. Corrosion consumes the iron with the growth of both  $\alpha\text{FeOOH}$  and, in chloride rich environments,  $\beta\text{FeOOH}$  as an outer skin. In this instance the electrolytes will comprise chloride compounds formed from the chloride provided by the marine environment where Peggy spent her life. Chloride will have been drawn into the iron as a counter ion in the corrosion process. When the water evaporates in drier atmospheres corrosion ceases and the outer skin forms a solid shell creating a hollow sphere. High humidity will reactivate the process and eventually large corrosion blisters form.

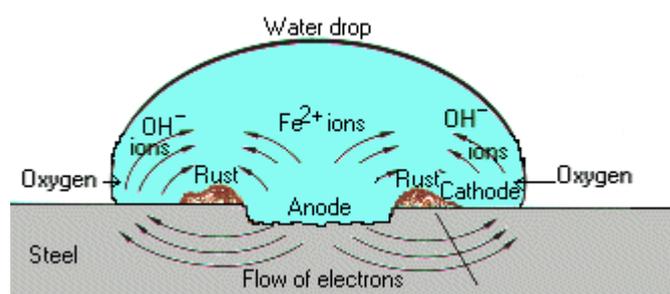
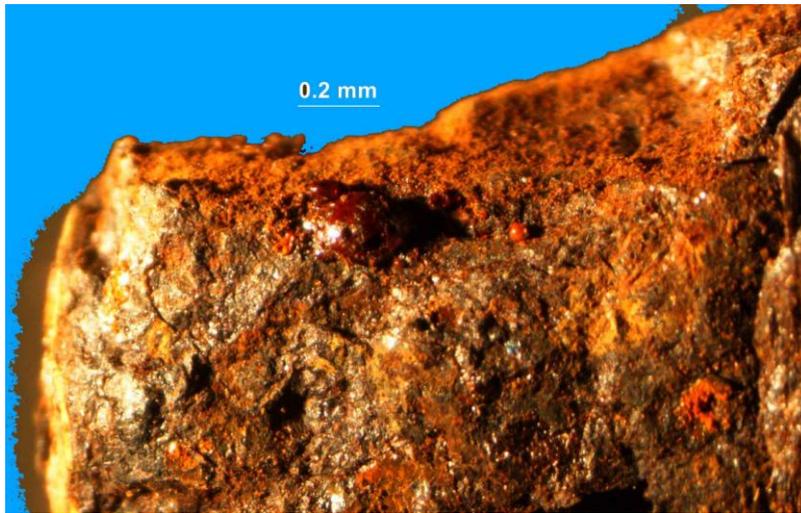


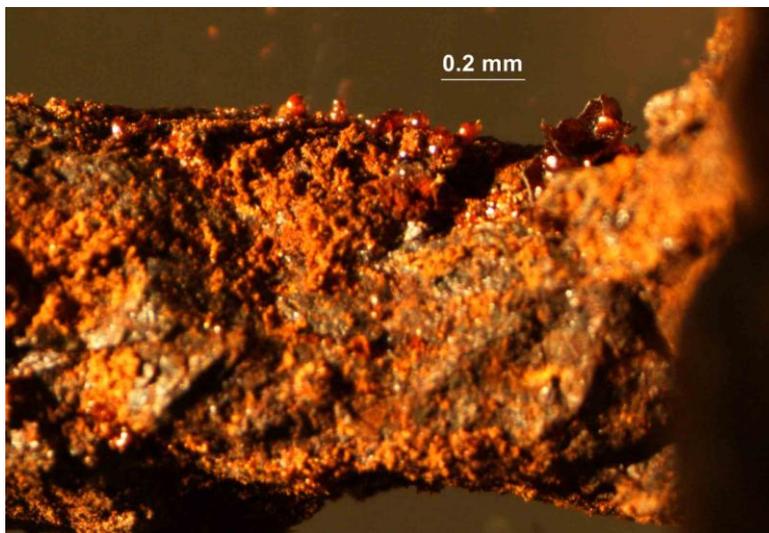
Figure 2. Pustule formation on iron objects

Both broken and unbroken shells can be seen on all the iron from the Peggy (figures 3-7). These have been activated in a high relative humidity prior to the nails being sent to Cardiff. Further evidence of active corrosion is the lamination of the corrosion layers from the remaining metal core seen in figure 8. Overall the physical integrity of the nails is compromised by extensive loss of metal with localised thinning evident in

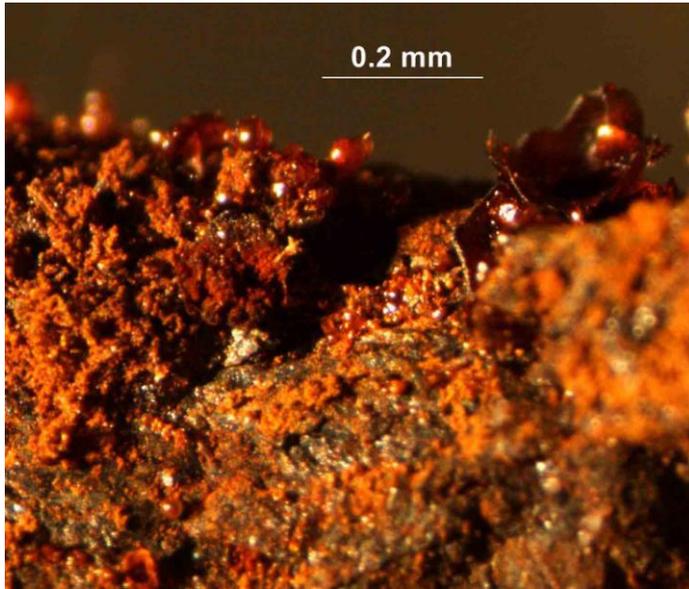
figure 8. This is likely to have occurred at an area where oxygen levels around the nail change from high to low.



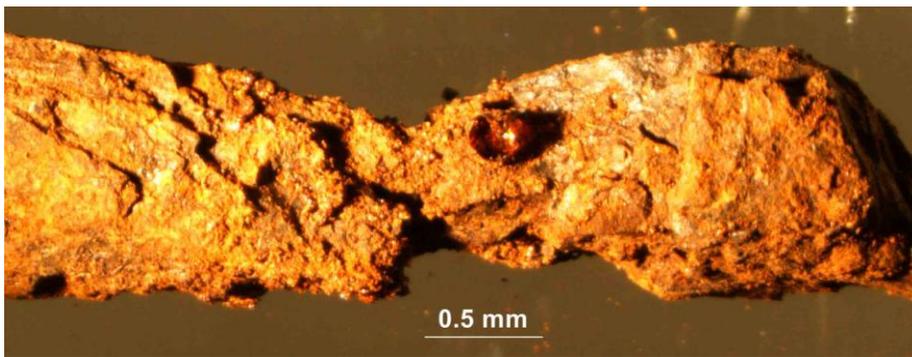
*Figure 3. Nail 0014/1: centre left is a well developed corrosion pustule (dark orange-red); to its right is a much smaller newly developing pustule (orange).*



*Figure 4. Nail 0014/2: large broken corrosion pustule is visible on the surface (top right). Elsewhere there are large numbers of corrosion pustules of all sizes and colours. The light orange pustules are in an early stage of growth. None of these are currently active due to the low relative humidity.*



*Figure 5. Nail 0014/2: close up of large broken corrosion pustule in figure 4. It is visible on the surface top right.*



*Figure 6. Nail 0014/3: broken corrosion pustule. There is extensive thinning of nail in centre compromising structural integrity.*



*Figure 7. Nail 0014/4: corrosion pustules.*

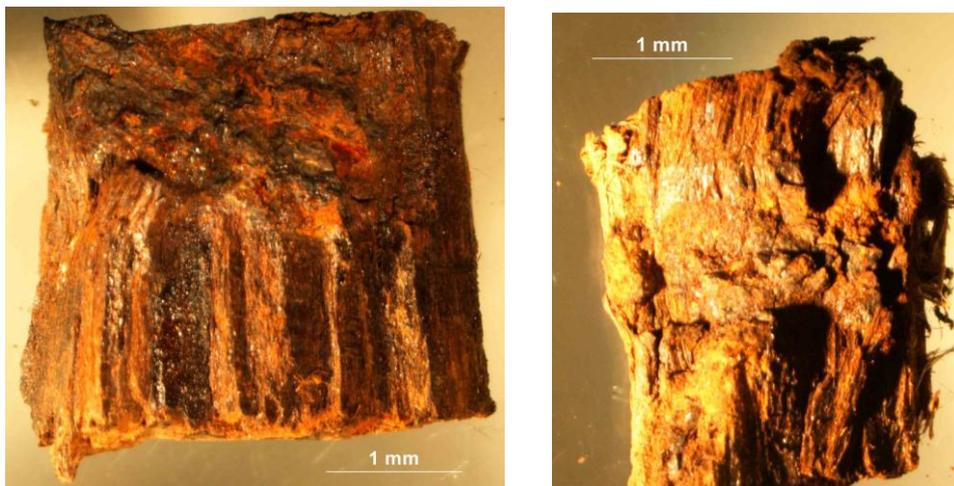


*Figure 8. Nail 0014/6: corrosion pustules and lamination of corrosion product at metal/corrosion layer interface.*

### **3.2 Conclusion on stability of nails using visual evidence**

Evidence from inspection suggests that all the nails examined contain extensive amounts of electrolyte and are highly unstable. They will corrode rapidly in humid environments. The presence of  $\beta\text{FeOOH}$  also means they will corrode at low humidities. This will slow appreciably at 30-35% relative humidity, but will not stop until relative humidities of less than 25% are reached. The nails are extensively corroded and have reduced physical integrity. Some nails retained very little metallic iron, while others did retain a metal core.

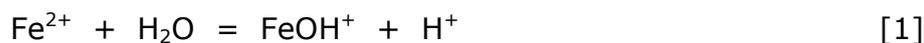
## **4 Examination of the wood**



*Figure 9. Wood sample on the lhs is showing signs of mineralisation. While the wood sample on the rhs is showing similar signs of mineralisation, it is less advanced, as it still contains fibrous wood fibres.*

The wood in the vicinity of the nails is infused with iron corrosion products and is beginning to mineralise (figure 9). The iron corrosion products are

hydrolysing the cellulose in the wood due to the acidity from hydrolysis of  $\text{Fe}^{2+}$  ions [1].



Acidity of the wood was tested by soaking small samples in 10 mls of deionised water and measuring their pH with a pH meter ( $\pm 0.1$  unit) (table 2).

The chloride content of these samples was tested using chloride content of the solution measured in ppm using a Research Machines PHM250 ion analyser. Buffer was added in the ratio 1:10. Concentration of chloride in the 11 ml solution was converted to  $\mu\text{g}$ . This was divided by sample weight to provide chloride content of wood as a function of sample weight (table 2).

Sample	Weight	pH	Chloride ppm (11ml sample)	Chloride content of wood $\mu\text{g}$ per gram of wood sample weight (ppm)
0014/1	0.158	6.2	41	2854
0014/2	0.297	5.4	148	5614
0014/3	0.290	5.1	244	9255
0014/4	0.802	5.2	592	8119
0014/5	0.280	5.3	136	5343

*Table 2. Acidity and chloride content of wood.*

The pH levels are all acid, signifying an acid environment in the wood around the nails. The soluble chloride fraction in the wood is high. After only 4 days soaking in the water the chloride concentrations in the wood ranged from 2854 ppm to 9255 ppm. These are above the total chloride content of many iron objects, as determined by their digestion. The fact that the chloride is extracted in water demonstrates the mobility of the chloride ions in moisture. This will offer a strong electrolyte around the iron nails in the wood in damp conditions. The chloride is also likely to be hygroscopic, attracting water to the wood. The microclimate around the nails is aggressive to iron.

## **5. Summary: Overview of analysis and discussion**

Corrosion of the nails could be stopped by placing the ship in a relative humidity of less than 15%, while the rate of corrosion of the iron could be much reduced by storage below 35% relative humidity. Above these values corrosion will increase as relative humidity rises and all the ingredients for rapid corrosion of iron are present around the nails: oxygen from the atmosphere; moisture in the air; chloride as corrosion products at the metal surface and in the wood surrounding the nail; low pH in the wood directly around the nail.

Acidity from the corrosion is hydrolyzing the wood in the immediate vicinity of the iron nails causing it to weaken and powder. This is exacerbated by the volume increase as metallic iron converts to iron compounds. The wood is infused with chloride, which is mobile and capable of forming a corrosive electrolyte around the iron. Some of the chloride salts present may be hygroscopic, but these were not identified in the analysis.

Realistically, the continued corrosion of the nails cannot be prevented, but it can be managed to decrease the rate of corrosion by reducing the amount of moisture in the ambient atmosphere. However, the implications of low relative humidity on the wooden hull are shrinkage and warping, while there is also the cost of such an exercise in outlay and energy to support its operation. The physical integrity of the nails is in question. They are much thinned and the time will come when they cease to perform their role in the hull. If their presence is central to the physical integrity of the hull, their replacement by a more stable fixing may be necessary.

## **6. Chloride content of nails.**

The chloride content in the nails could be examined by digestion of the nails. This will confirm their instability by recording the amount of chloride present in the nail, but cannot provide quantitative corrosion rate data. The chloride content of the wood around the nails already indicates that the chloride within the nails will be high and this is supported by microscopic examination of the nails, which indicates their instability. In view of the lack of rate data that analysis would provide, it is not recommended for adding any further information on stability.

## **References**

- CHANDLER, K.A. (1966). The influence of salts in rusts on the corrosion of the underlying steel. *British Corrosion Journal*, 1: July, 1966.
- EVANS U.R. and TAYLOR C.A.J. 1974 Critical Humidity for rusting in the presence of sea salt. *British Corrosion Journal* **1** 26-28.
- FELL V and WILLIAMS 2004 Monitoring archaeological and experimental iron at Fiskerton, England. *Metal 04 Proceedings of the international conference on Metals Conservation*. Ashton J and Hallam D. (eds) Canberra Australia 4-8 October 2004. 17-27 National Museum of Australia.
- GILBERG M.R. and SEELEY N.J. 1981 The identity of compounds containing chloride ions in marine iron corrosion products: a critical review. *Studies in Conservation* **26** 50-6.
- JONES, D. 1992 Principles and Prevention of Corrosion. Macmillan. New York.
- KNIGHT B. 1990 A review of the corrosion of iron from terrestrial sites and the problem of post-excavation corrosion. *The Conservator* **14** 37-43.
- MACLEOD I. D. 1991 Identification of corrosion products on non - ferrous metal artifacts recovered from shipwrecks. *Studies in Conservation* **36** 222 - 234

- NEFF D et al. 2004 Structural characterisation of corrosion products on archaeological iron. An integrated analytical approach to establish corrosion forms. *Journal of Raman Spectroscopy*, 35 issue 8-9 Aug-Sept , 739-745.
- NEFF D, DILLMANN, P., BELLOT-GURLET, L. and BERANGER, G. 2005 Corrosion of iron archaeological artefacts in soil: characterisation of the corrosion system. *Corrosion Science* 47, 515-35.
- RICHARDSON, G.M. and MALTHUS, R.S. (1955). Salts for Static Control of Humidity at Relatively Low Levels. *Journal of Applied Chemistry* 5, 557-567
- SELWYN LS, SIROIS PJ and ARGYROPOULOUS V 1999 The corrosion of archaeological iron with details on weeping and akageneite. *Studies in Conservation* **44** 217-232
- SPENCER, H.M. 1926. International Critical Tables 1 67. New York: McGraw-Hill.
- TRETHEWEY K. and CHAMBERLAIN J. 1988 Corrosion for Students of Science. Longmans
- TURGOOSE S. 1982b Post excavation changes in iron antiquities *Studies in Conservation* **27** 97-101.
- TURGOOSE S. 1982a The Nature of Surviving Iron Objects. Conservation of Iron (eds) Clarke R and Blackshaw S (eds) National Maritime Museum, Monograph No. 53, pp 1-8.
- WATKINSON D.E. 1983 Degree of mineralisation: its significance for the stability and treatment of excavated ironwork *Studies in Conservation* **28** 95-90.
- WATKINSON D. and LEWIS M., 2005a Desiccated storage of chloride contaminated archaeological iron objects. *Studies in Conservation*. 50 241-252
- WATKINSON D. and LEWIS M.R.T., 2005b The Role of  $\beta\text{FeOOH}$  in the Corrosion of Archaeological Iron, in Materials Issues in Art and Archaeology VII, edited by Pamela B. Vandiver, Jennifer L. Mass, and Alison Murray (Mater. Res. Soc. Symp. Proc. **852**, Warrendale, PA, 2005), OO1.6
- WATKINSON, D. and LEWIS M., 2004. ss Great Britain iron hull: modelling corrosion to define storage relative humidity. *Metal 04 Proceedings of the international conference on Metals* Conservation. Ashton J and Hallam D. (eds) Canberra Australia 4-8 October 2004. 88-103 National Museum of Australia.
- ZUCCI F., MORIGI G. & BERTOLASI V. 1977 Beta iron oxide hydroxide formation in localised active corrosion of iron artifacts. In: *Corrosion and Metal Artifacts: A dialogue between Conservators, and archaeologists and Corrosion Scientists*. Brown F. B.(ed) National Bureau of Standards Special publication 479.