Section 4

Composite Artifacts

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Characterisation of metal threads in Renaissance tapestries

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Abstract

The MODHT (Monitoring of Damage in Historic Tapestries) project investigated the history, composition and deterioration of metal threads with a textile core.
Metal thread manufacture has been investigated by Scanning Electron Microscopy (SEM) and characteristic deformations established on historic and "model" metal threads. Rare examples of triple wrapped silver gilt threads were observed in some 16th century tapestries of the Royal Spanish collection.
SEM, Energy Dispersive X-ray analysis (EDX), X-ray Photoelectron Spectroscopy (XPS) and depth profiling Secondary Ion Mass Spectrometry (SIMS) were utilized for chemical compositional analysis of the metal layers and alloys and the corrosion products of original metal thread samples.
Accelerated tarnishing tests on silver and copper were performed to determine the influence of the degradation of the dyed wool and silk fibres on the formation and composition of corrosion products.
Metal threads and aged metal foils were analysed by SEM in order to establish the morphology of corrosion growth due to natural and accelerated ageing.

Keywords: metal thread, gold layer, tapestry, corrosion, XPS, SIMS

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1. Introduction

1.1 History of metal threads

Decorative metals have been incorporated into textiles for thousands of years, with an early reference found in the Old Testament, Exodus 39:2-3; approximately 12th to 13th centuries BC.

The earliest metal threads were thin strips of gold, which were cut from a beaten metal foil and directly woven or embroidered into textiles. Later these strips were wound around a fibrous core; this would introduce more flexibility to the thread and make its uses more versatile. The core fibres were usually silk, dyed according to the colour of the metal wrapping, e.g. yellow or red for gold threads, undyed white silk for silver threads; though metal threads with a linen, cotton, animal hair or sinew core have also been reported (Braun-Ronsdorf 1961; Budney and Tweedle 1985; Indictor and Blair 1990; Skals 1991). Early examples of wound metal threads are a 3rd century textile fragment found in a Roman sarcophagus in Hungary (Geijer and Thomas 1964-65) and the 4th century remains of gold filament wrappings from the grave of a woman at London's Spitalfield market (King 2003).

Published data on surviving threads from the 12th century and before suggest that either pure gold or alloys with a very high gold content were used (Braun-Ronsdorf 1961; Jaro 1990; King 2003). It is not clear when silver or silver-copper gilt metal threads were first introduced but most surviving threads of the late Medieval and Renaissance period are of that type (Hoke and Petrascheck-Heim 1977; Darrah 1987; Garside 2002; Hacke et al. 2003).

Early metal threads were "beaten and cut", where a single sided gilt block of silver or silver alloy was beaten into thin foils, cut into narrow strips and joined to filaments. Later the expansion of wire manufacturing encouraged the production of metal filaments; a cast silver or silver alloy rod was gilt and drawn through die holes of successively decreasing diameters. The wire was then flattened between rollers; hence "cast, drawn and rolled". This produced a metal filament with double sided gilding. The earliest account of wire making with draw-plates was given by Theophilus in the early 12th century (Oddy 1977). Towards the end of the 14th century production centres in Italy and Spain took up the manufacture of cast, drawn and rolled metal threads (Braun-Ronsdorf 1961) and from the late 15th until the 17th century this technique gradually replaced the beaten and cut method in Europe (Jaro et al. 1990; Montegut et al. 1992; Jaro et al. 2000; Garside 2002; Tronner et al. 2002).

There were several possible methods of gilding the blocks or rods of silver; the earliest is believed to involve hammering the gold onto the silver surface, while later methods included soldering, welding or fire-gilding with mercury amalgam (Hoke and Petrascheck-Heim 1977; Schreier and Bresee 1979; Jaro et al. 1990; Jaro and Toth 1994).

In the 11th or 12th century the so called “Cyprus gold” began to spread to Europe from Byzantium, western Asia or northern Africa through the ports of Cyprus (Braun-Ronsdorf 1961). Cyprus gold was a membrane thread, based on a gilt leather or animal gut filament wound around a fibrous core. Membrane threads of Chinese or Japanese origin usually had a paper substrate (Darrah 1987). Membrane threads are more flexible and lighter than solid metal threads but regarded of inferior quality due to the fragility of the gold layer to abrasion and the lower luster compared to solid metal threads. By the 13th or 14th century production of membrane threads was also developed in Europe but their importance declined by the 16th century. The most common gilding technique was the application of gold leaf (Jaro et al. 1990), possibly with animal glue or fat as an adhesive (de Reyer et al. 2002).

Determination of the manufacturing technique is often made by means of SEM analysis of the edges of metal threads. Sharp angles with tool marks left from cutting indicate “beaten and cut” threads, while smooth and round edges and longitudinal striations are characteristic for “cast, drawn and rolled” threads. However, SEM analysis of model metal threads, produced, in this study, from flattened (rolled) wires, showed that this characterisation can be misleading. Figure 1 shows the edges on the model metal threads were also often rough with sharp angles. Therefore, an unambiguous determination of the manufacturing technique is limited to the analysis of metal filaments with single- or double- sided gilding.

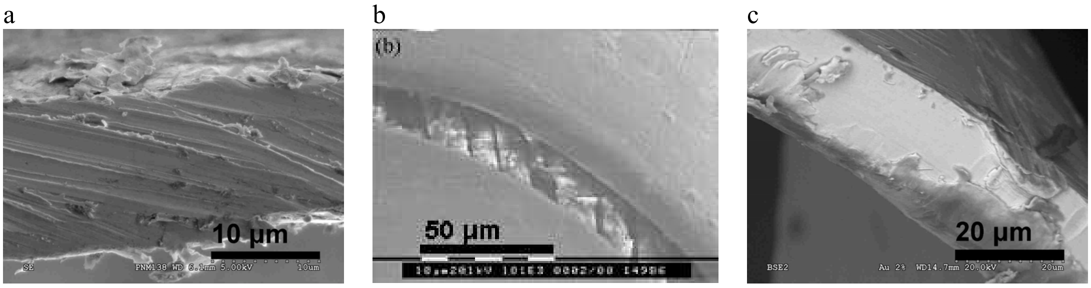


Figure 1. SEM micrographs of edges of metal threads. a: “beaten and cut”, b:”cast, drawn and rolled”, c: model metal filament

1.2 Description of metal threads in this study

The metal threads investigated in this study were taken from five European Renaissance tapestries; their details of origin and manufacture are listed below:

- ‘Abraham and Melchizedek’ (HCP), Hampton Court Palace, woven by Willem de Kempeneer in Brussels, ca. 1535, 112 metal thread samples taken.
- ‘Christ before Pilate’ (BXL2), National Museum, Brussels, woven in Brussels, ca. 1520, 21 metal thread samples taken.
- ‘Dédalo e Ícaro’ (PNM1), Patrimonio Nacional Madrid, Wilhelm van Pannemaker, Brussles, ca. 1545, 27 metal thread samples taken.
- ‘Júpiter y Ganimedes’ (PNM2) Patrimonio Nacional Madrid, Wilhelm van Pannemaker, Brussles, ca. 1545, 17 metal thread samples taken.
- ‘Neoptolemo y Polixena’ (PNM5) Patrimonio Nacional Madrid, Wilhelm van Pannemaker, Brussels, ca. 1545, 15 metal thread samples taken.

The thread diameter, width of metal foil and number of coils per 5 mm thread were measured manually through digital imaging analysis. All µm measurements were rounded to the nearest 50 due to the relative imprecision of the measurement technique.

All metal thread samples in this study consist of solid metal strips wound around a silk core, which is white or light yellow for silver threads and dyed in darker yellow shades for gilt threads. All but one sample exhibit S twist direction of the metal coils and are categorized according to thread diameter and colour of metal strip in Table 1. The metal strip width and number of coils per unit length were found to vary with thread diameter. Large diameter threads (≥ 700 µm) generally have wider metal strips and fewer coils than medium (< 650 > 350 µm) or small diameter threads (≤ 350 µm), which show the finest metal strip width, the most coils per unit length and are also the least corroded, Figure 2. The relationship between diameter, width and coil number was also observed in the silver threads and those that were heavily corroded.

Table 1. Categorization of metal threads from five MODHT Renaissance tapestries.

Group	**Number of samples in tapestry**					
	HCP	PNM1	PNM2	PNM5	BXL2	Total
gilt large diameter (≥ 700 µm)	14	-	-	-	-	14
gilt medium diameter (< 650 > 350 µm)	25	3	3	5	10	46
gilt small diameter (≤ 350 µm)	11	6	6	3	-	26
gilt corrosion	19	7	3	-	4	33
silver	26	4	4	1	-	35
double wrapped	12	4	2	1	-	19
triple wrapped	-	1	-	3	-	4
restoration	-	-	1	-	7	8
no assignment	5	2	-	1	-	8
Total number of samples in tapestry	112	27	17	14	21	193

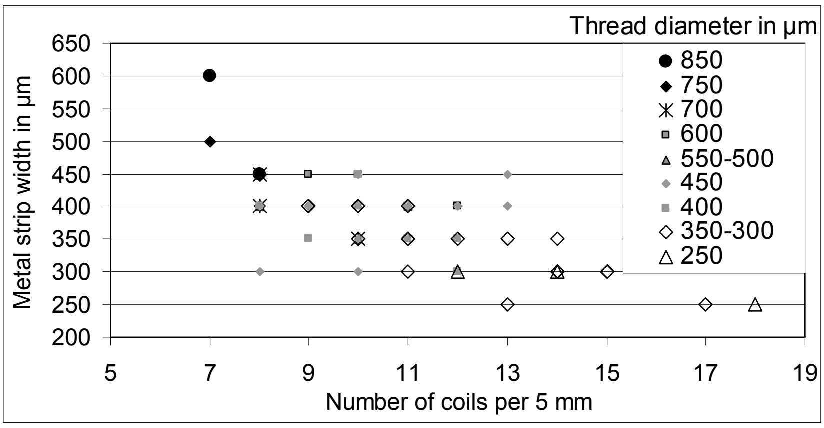


Figure 2. Relationship of metal thread diameter, metal strip width and number of coils per unit length of metal thread (67 samples).

A total of 23 threads with two or even three layers of metal wrapping were found in samples of four out of the five tapestries studied. Metal threads with multiple wrapping have rarely been mentioned in the literature (Hacke et al. 2003). Two double wrapped gilt leather substrate metal threads with linen and cotton cores were found in a 14th century Near Eastern textile (Indictor et al. 1988). Montegut mentions one double wrapped thread from late 15th century Spain or Italy, possibly Venice (Montegut et al. 1992), while Indictor identified one double wrapped metal thread of Indian origin (Indictor and Blair 1990). Figure 3 shows samples of triple wrapped threads; the abundance of precious metal, their intricacy and evenness of structure is striking, indicating that these are threads of premium value, used only in textiles of the highest quality such as tapestries of the Abraham series commissioned by Henry VIII and the tapestry series of the Fables of Ovid in the Royal Spanish collection.

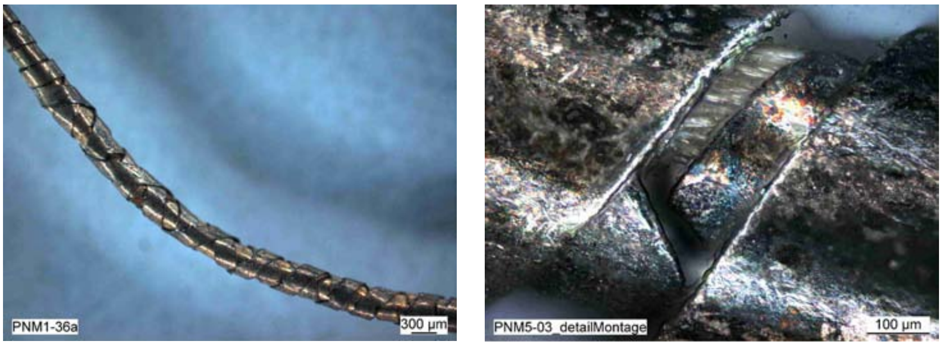


Figure 3. Triple wrapped metal threads.

Metal threads in tapestries are in close proximity to wool and silk and it has been suggested that the degradation of textile fibres influences the tarnishing of metals (Hoke and Petrascheck-Heim 1977; Howell et al. 1999). This study investigates the corrosion products on metal coupons tarnished by accelerated ageing, as well as historical metal threads. The combination of X-ray Electron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS) and Secondary Electron Microscopy coupled with Energy Dispersive X-ray analysis (SEM/EDX) have been applied to investigate the bulk and surface metal alloy contents and corrosion products. These techniques have been previously used to study metal threads and provide a powerful complementary approach to characterise surface and sub-surface composition and morphology (Howell et al. 1999; Hacke et al. 2003).

2. Experimental techniques

2.1 Accelerated tarnishing

Silver and copper coupons, 5 x 10 x 0.25 mm, > 99.9 % purity, were cut and a pin hole punched in each to allow suspension during the Oddy tests. The coupons were cleaned successively in propanol, hexane, chloroform and methanol for 10 minutes in an ultrasonic cleaner. Silver and copper coupons were incubated under thermal or light Oddy test conditions indicated below with the following wool and silk samples: undyed, dyed with weld, woad, madder or brazil.

2.1.1 Thermal Oddy test

0.2 g of wool or silk yarn was placed in the bottom of a test tube together with Durham tubes (6.5 x 30 mm) filled with deionised water. Silver and copper coupons were suspended from the top of the test tube using nylon filament and the tubes were sealed with a stopper and tape. 12 yarn samples and one control were incubated at 60°C for 4 weeks.

2.1.2 Light Oddy test

Wool and silk fabrics, 4 x 5 cm, were stapled to a cardboard backing and placed in glass cells (2 x 5 x 15 cm) along with tubes, 6.5 x 120 mm, filled with deionised water. Silver and copper coupons were suspended from the top of the cells containing the fabric pieces and one control sample containing only the tube with deionised water. The coupons were shielded from direct irradiation with cardboard placed around the top of the sealed cells. The fabric samples were irradiated for 300 hours using an OSRAM 400 W HQ (MB-U) mercury lamp in a Microscal Ltd. Mark V Light Fastness Tester. The cells were equipped with a circulating water cooling system maintaining the temperature at 27-29 °C.

2.2 SEM/EDX

The samples were examined with a Hitachi SEM S-3000N / EDAX system, using the secondary electron detector, a medium aperture, approximately 40 spot size, a working distance of ~ 5 mm and a 5 keV accelerating voltage were used for all samples. EDX spectra were obtained at a 15 mm working distance and a 25kV accelerating voltage. Quantification was performed using background subtraction and ZAF correction.

2.3 XPS

Spectra of metal coupons were obtained on a Kratos Axis Ultra X-ray photoelectron spectrometer using the Al Kα monochromator X-ray source, with a pass energy of 80 eV for wide scans and 20 eV for high resolution scans. The analysed area was approximately 300 x 800 μm. Metal threads were analysed on a SSX-100 ESCA Spectrometer using monochromated Al Kα X-rays, 152 eV pass energy and 150 μm spot size. All data was processed using Casa XPS 2.2.80 software. Quantification was performed using appropriate relative sensitivity factors, transmission functions and a linear background.

2.4 SIMS

Metal threads were analysed using a CAMECA IMS 4f Magnetic Sector SIMS instrument. The Cs+ primary ion beam was operated at 10 keV, with a beam current of 0.1-0.4 nA for positive and negative mass spectra, and 20 nA for positive depth profiles. The areas analysed were 250 μm^2 for spectra and 100 μm^2 to 200 μm^2 for depth profiles. Typical acquisition times were 300 s for spectra and 3000 s for depth profiles. A reference crater was measured using a Detak Profilometer; subsequent depth calibrations were based on a sputter rate factor. Semi-quantitative values were calculated as relative atomic % assuming the same ionization probabilities for $CsAg^+$, $CsCu^+$ and $CsAu^+$ and correcting for the natural isotopic abundances.

3. Results and Discussion

3.1 Alloy composition of metal threads

SIMS positive ion depth profiles have been obtained from all metal thread exterior sides and one interior side only. Figure 4 shows a typical depth profile of the exterior of a gilt metal thread. The initial intensities for contaminants such as C, K, Cl and Na containing compounds is high but decreases rapidly as the sample surface is etched. In sample PNM5_24 the gold intensity reaches its maximum at a depth of approximately 20 nm, and its minimum, i.e. bulk intensity at 200 nm. Other samples had the gold layer interface between 100-500 nm (PNM2_19) and 40-300 nm (PNM1_38). These values are consistent with other recent studies on metal threads, which revealed lower gold layer thicknesses than previously proposed (Enguita et al. 2002; Tronner et al. 2002).

Chlorine and sulphur ions are probably derive from corrosion compounds and showed a lower rate of decrease than other contamination residues. The lower intensity of $133Cs_2 32S^+$ compared to $133Cs_2 35Cl^+$ was attributed to the lower sensitivity of positive ion SIMS to sulphur. Sulphur compounds showed higher intensities in negative ion SIMS mass spectra and XPS analysis indicated similar atomic concentrations of chlorine and sulphur.

With some samples a second contaminant maximum (CN, Ca, NaCl and KCl) was observed at the interface between the bulk metal and surface gild layer and possibly originated from handling of the silver – copper alloy prior to gilding or from precipitation of contaminants through the corrosion layer and faults in the gold layer.

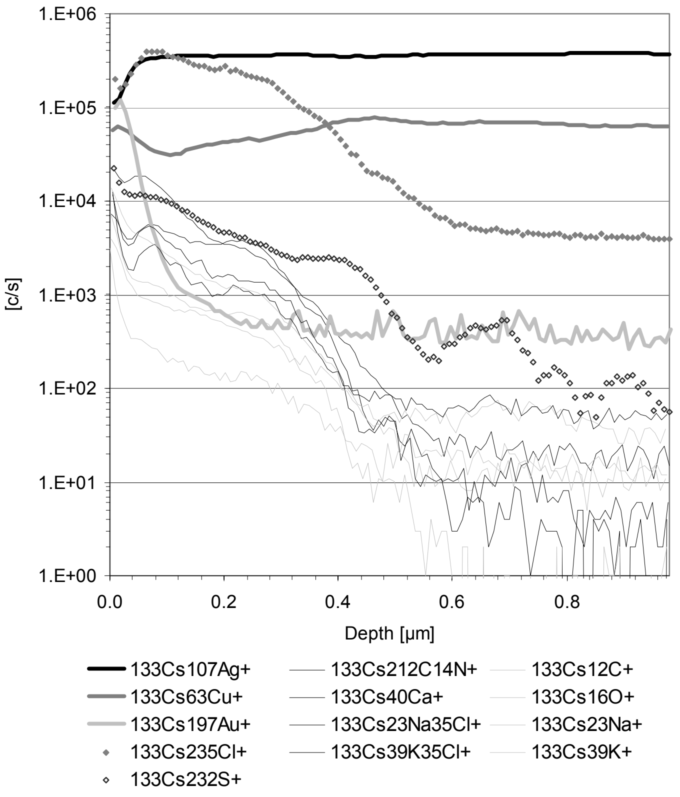


Figure 4. SIMS positive ion depth profile of the exterior of metal thread PNM5_24

The SIMS, XPS and EDX analyses present values in relative atomic % of metallic components only, Table 2. EDX, at 25 kV accelerating voltage, has a depth analysis of > 0.2 µm, while XPS probes the surface to a depth of < 10 nm and SIMS depth profiles in the range of 0 to 2 µm. All PNM samples showed gilding on the exterior side only, with the highest Au concentrations in the PNM5_24 sample. The concentrations of copper and silver exceeded that of gold on the surface and throughout the gold layer of all samples indicating that the surfaces were not gilt with pure gold but with silver – copper – gold alloy or the alloy formed during gilding or the silver and copper ions precipitated through the gold layer. Precipitation of Ag and Cu ions was also supported by the XPS results, which showed low gold concentrations at the outer surface. The SIMS depth profile of the interior of PNM1_38 showed the highest copper concentration near the surface and decreased with increasing depth to the bulk value determined with the exterior face analysis. Previous SIMS depth profile analyses of the interior of single sided gilt metal threads showed similar results (unpublished analyses of MODHT samples), suggesting copper ion migration towards the surfaces of the metal filament.

BXL2_15 had comparatively low gold concentration and showed no substantial decrease of contaminations throughout the depth of analysis by SIMS (maximum depth was 2 µm). This was attributed to the very uneven and damaged surface. The metal filament proved very brittle when unwinding it from the silk core and SEM analysis revealed a heavily corroded, broken and delaminated surface. The metal thread also differed from the other samples by having a very low copper concentration.

Table 2. EDX, XPS and SIMS positive ion depth profiling analyses of the alloy compositions of exterior and interior surfaces of metal threads.

Analysis	Sample	External relative atomic%			Internal relative atomic %		
		Ag	Cu	Au	Ag	Cu	Au
EDX							
	PNM1_38	83.2	9.6	7.3	84	16	0.0
	PNM2_19	75.5	15	9.5	88	12	0.0
	PNM5_24	80.3	8.8	10.9	88.5	11.5	0.0
	BXL2_15	98.7	0.0	2.7	92.2	4.6	3.3
XPS							
	PNM1_38	79.5	15.8	4.7	76	24	0.0
	PNM2_19	82.1	17.5	0.4	67.9	31	1.1
	PNM5_24	85.9	11.8	2.3	63.8	36.2	0.0
	BXL2_15	96.9	0.0	3.1	92.8	7.2	0.0
SIMS (external crater 0 µm and maximum depth of analysis 0.5-2 µm)							
	PNM1_38	59.95	29.53	10.52	88.94	11.05	0.01
	PNM2_19	73.8	25.4	0.8	92	7.8	0.2
	PNM5_24	61.68	18.33	19.99	89.61	10.36	0.03
	BXL2_15	93.17	1.31	5.52	98.71	0.42	0.87
SIMS (internal crater 0 µm, Cu max 0.14 µm and maximum depth 1.8 µm)							
	PNM1_38				88.8	11.1	0.0
					83.8	16.1	0.1
					88.0	11.9	0.0
SIMS (external crater Au max, 0.02-0.1 µm)							
	PNM1_38	61.1	24.4	14.5			
	PNM2_19	70.3	20.9	8.8			
	PNM5_24	60.17	15.83	24			
	BXL2_15	90	0.6	9.4			

3.2 Accelerated tarnishing and corrosion on metal threads

Both thermal and light Oddy tests produced visible tarnishing on the Ag and Cu coupons incubated with the textile samples, but none on the control coupons. Ag and Cu coupons incubated with wool showed significantly more discolouration than those coupons incubated with silk. This was expected due to the higher levels of sulphur containing amino acids in wool than silk. Discolouration was more obvious on Ag than on Cu and most evident around the edges of the coupons. Thermal degradation of the dyed fibres produced similar levels of tarnish with blue to black shades observed. However, greater variation was observed due to the photo degraded dyed fibres. The undyed wool was the only sample that caused complete blackening of the Cu coupon, while all other wools caused patchy black corrosion. The silk caused no visible tarnish on Cu. Tarnish on the silver coupons was observed at varying shades of yellow, green, red, purple, blue and black. There was a gradation of tarnish from yellow and red at the centre of the coupons, to blue or black at the edges of the metal coupons, suggesting that the different colours were caused by varying tarnish film thicknesses rather than chemical composition of corrosion products. Table 3 lists the observed tarnish colours on both sides of the metal coupons subjected to photo degradation of the differently dyed fibres. Although all fibres caused the tarnishing of silver coupons, woad and madder dyed wool, and undyed silk appeared to cause the highest levels of tarnish. The tarnishing of the dyed wool samples may be due to greater light absorption of the dark shades increasing sulphur volatilisation, while with silk the nature of the effect is at present unclear.

Table 3. Colour variation of tarnish on Light Oddy tested silver coupons.

Textile material		Side A*		Side B*			Legend
Control		0	0	0	0		0 = no tarnish
Silk	undyed	5	4	1	4		1 = yellow
	weld	3	5	1	3		2 = green
	woad	5	1	1	5		3 = red
	madder	3	1	1	5		4 = purple
	brazil	3	3	1	3		5 = blue
Wool	undyed	0	6	2	2		6 = black
	weld	2	2	2	2		
	woad	5	1	4	1		
	madder	5	4	3	6		
	brazil	1	5	2	2		

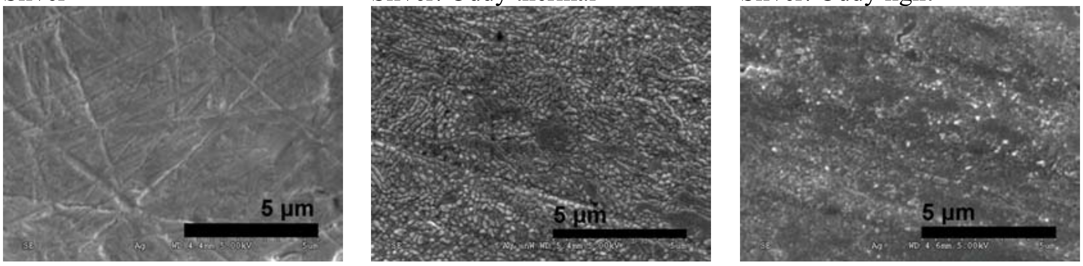
* number for dominant tarnish colour is stated first

SEM micrographs of the corrosion morphologies on silver and copper are shown in Figure 5. In areas with little corrosion the initial growths were found to develop along scratches and pits on the surface. Generally the corrosion growths on copper were more rounded and accumulated than corrosion on silver, which formed a more evenly distributed layer with uniformly sized corrosion crystals and little differences in height. In addition, some of the copper coupons associated with photodegradation of wool showed regular longitudinal crystals.

The morphological appearance copper sulfide corrosion on metal threads has been described as "trees", "bushes" or "black spot disease", while silver sulfide crystals have been described as "dendrites" breaking the gold layer (Hoke and Petrascheck-Heim 1977), "whiskers", "black fuzzies", "flower-or tree-shaped" and "mushroom-shaped bubbles" (Jaro and Toth 1997). While these descriptions are subjective, there does seem to be a clear distinction between sharp and rounded crystals. The cause for the different growth behaviour of the sulphide crystals is unknown. Corrosion morphologies on metal threads in this study were found to be rounded crystals, Figure 6. Corrosion cracking, flaking and delamination were observed on all samples, particularly BXL2_15.

Delamination and differences in the cracking structure have previously been attributed to either stress-corrosion causes, or the manufacturing technique, for example folding and stretching of a metal foil or strip prior to cutting into narrower strips for winding (Jaro and Toth 1997), or joining of thin foils by hammering and subsequent cutting into strips (Hardin and Duffield 1986). However, corrosion growth in layers and cracking of corrosion crystals has been observed on heavily corroded samples of the modern Oddy tested coupons, Figure 5.

Silver Silver: Oddy thermal Silver: Oddy light



Copper Copper: Oddy thermal Copper: Oddy light

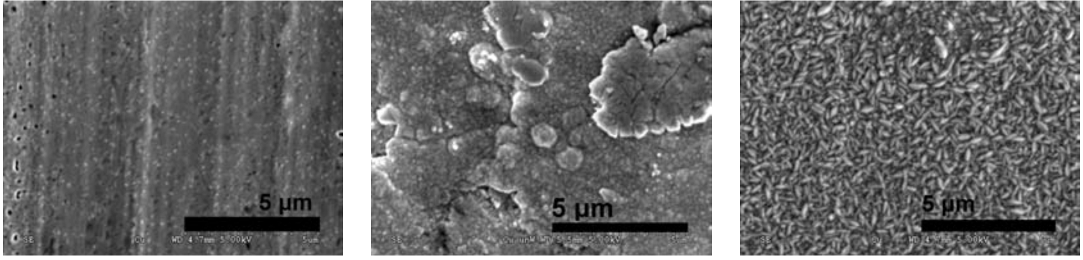
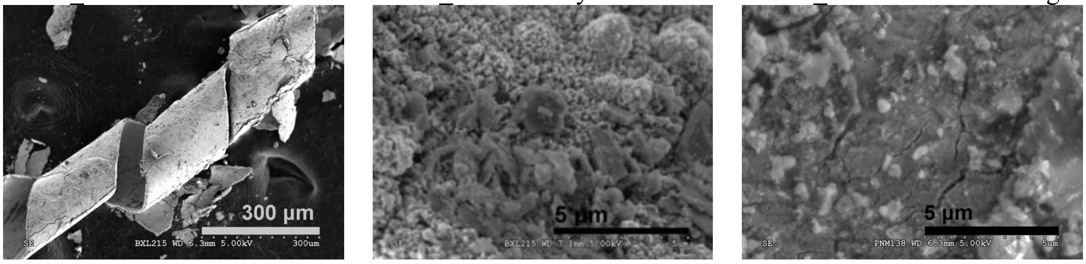


Figure 5. Corrosion crystal morphology on Thermal and Light Oddy tested silver and copper coupons.


BXL2_15 delamination BXL2_15 round crystals PNM1_38 corrosion cracking

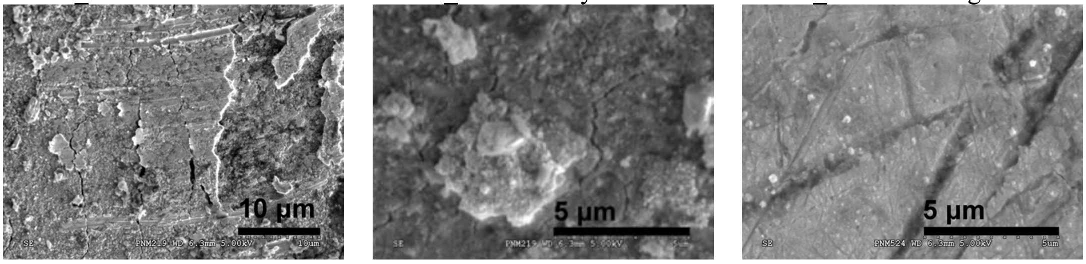

PNM2_19 delamination PNM2_19 round crystal PNM5_24 scratched gilt surface

Figure 6. Corrosion on metal threads.

XPS analysis of the coupons showed that the relative levels of oxygen and carbon were significantly higher on copper coupons than on silver coupons, with the atomic ratio O/Cu being ~ 2.5 and C/Cu ~ 5, while O/Ag was ~ 0.5 and C/Ag ~ 1.3. These ratios did not change significantly due to the accelerated tarnishing tests. Other low level contaminants were chlorine and nitrogen. Only the sulphur to metal atomic ratios showed significant increases due to accelerated tarnishing, Table 4. Both the sulphur atomic % and the atomic ratios of sulphur to metal were higher on silver than on copper, and were also higher due to the degradation of wool than silk. This agreed with the visual assessment of levels of tarnishing. The sulphur levels were higher on those metal coupons exposed to light irradiated wool and silk compared to thermally degraded wool and silk. This could be due to the relative exposure periods or the greater degradation of the light.

XPS high resolution scans of the S (2p) peaks showed that sulphur was mainly present in its S^{2+} form; only small amounts of S^{6+} were detected on copper coupons, probably as sulfates, Figure 7. The maximum atomic sulphur to metal ratios were > 0.5 indicating that sulphur was present not only as Ag_2S and Cu_2S, which would yield maximum ratios of 0.5 if the whole metal surface was converted to sulfide. The nature of this additional sulphur concentration is at present uncertain. However, future research will focus on establishing the nature of the corrosion layer, its durability to aqueous washing and possible detergent adsorption on clean and corroded surfaces.

XPS analysis of metal threads showed the presence of sulfide on all samples, and low levels of sulfate on PNM2_19 only. Chlorine was also present on all samples, usually in similar concentrations to the sulphur. The highest ratios of sulphur to metals were detected on the interior of BXL2_15, where atomic % S/(Ag+Cu) = 0.34.

Table 4. Relative sulphur levels on tarnished Oddy tested silver and copper coupons.

Oddy test set	Test material	Atomic % ratio	
		S/Cu	S/Ag
Thermal	Control	0.05	0.07
	Silk	0.04-0.09	0.16-0.22
	Wool	0.13-0.39	0.35-0.51
Light	Control	0.09	0.09
	Silk	0.19-0.33	0.39-0.59
	Wool	0.43-0.67	0.44-0.62

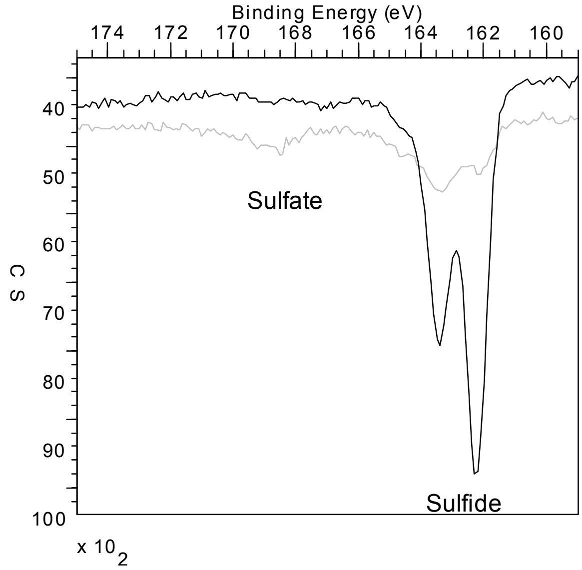


Figure 7. XPS high resolution scans of S (2p) on Light Oddy tested copper coupons incubated with undyed silk – and undyed wool –.

4. Conclusions

Measurements of gilt metal threads from Renaissance tapestries indicate a correlation between metal thread diameter, metal strip width and the number of coils per unit length of thread. Those threads with the smallest diameter (< 350 µm) and most coils (> 10 per 5 mm) appeared to be of "superior" quality. Rare triple wrapped metal threads were reported for the first time observed in tapestries belonging to the set of the "Fables of Ovid" of the Royal Spanish collection, manufactured in Brussels, 1545.

SEM micrographs of silver and copper coupons incubated with wool or silk and exposed to heat or light irradiation showed variations in corrosion morphologies, particularly of the copper and silver sulfides. XPS analysis of accelerated tarnished coupons and corrosion products on metal threads confirmed the presence of mainly sulfide corrosion with some sulfate and chlorine residues also on the metal threads.

SIMS analysis indicated the presence of thin surface gilt layers with gold concentration maxima at depths of 20 – 100 µm. Combined EDX, SIMS and XPS analyses of silver and copper suggested metal ion migration and/or application of a gold alloy rather than pure gold to the silver - copper alloy substrate.

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Electrolytic stabilisation of a marine composite porthole and its framework

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Abstract

Often the treatment of a composite metal artefact that cannot be dismantled requires a compromise as regards the conservation of all the materials involved. While treating one material it is difficult to assure that the others are not affected. With this paper we propose a methodology for the safe electrolytic stabilisation of a marine composite metal artefact (a porthole and its framework) constituted mainly of graphitized grey cast iron elements associated with other materials such as copper, glass, rubber and paint. The methodology comprises the determination of the parameters of treatment with metal coupons simulating the behaviour of real artefacts, together with the use of basic electrolytic equipments that are normally available in a conservation laboratory.

After the description and condition survey of the artefact, the coupons are used to determine the ranges of electrolytic parameters that are suitable for the stabilisation of the artefact in a non buffered 1% (w/v) $NaNO_3$ solution. Emphasis is put on the stability of the pH during the stabilisation process to assure the protection of all the materials.

Keywords: Composite metal artefacts, electrolytic techniques, stabilisation in neutral solution, monitoring of parameters, transfer of knowledge

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1. Introduction

This project started while the two authors were both staying in Finland, at the Conservation Department of EVTEK, Institute of Art and Design, Vantaa. This institute had previously established a Master's degree in the conservation of marine artefacts, and during that period a conservation laboratory had been specifically equipped to treat artefacts recovered from the sea.

One aspect of the project consisted in a transfer of knowledge on electrolytic techniques used for the conservation of metal artefacts. Some artefacts could be easily treated since protocols already existed (stabilisation of iron or copper based artefacts). Others needed a new approach that required the participation of both a conservator and a conservation scientist. Composite artefacts are typical of these complex objects that raise either ethical issues such as the need to treat the artefact as a whole (without dismantling it) and/or technical ones such as the conservation of the original materials (that might get damaged during the treatment). The porthole and its framework provided to the institute by Mr. Mika Pohjonen, private diver, were challenging enough to be considered as case studies within this transfer of knowledge exercise. To date only a few composite artefacts have been treated with electrolytic techniques (Degrigny 2001, Monluçon & Lacoudre 1988). Most of the time these composites contain waterlogged organic materials and specific protocols have to be developed (Degrigny & Guilminot 98, Guilminot 2000). In this project we wanted to concentrate on non-waterlogged materials for which the literature is more scarce.

1.1 Description of the artefact

The object was raised out of *the Rhein* shipwreck, which had sunk in 1958 in the Baltic Sea near Utó (West-coast of Finland), and was left exposed outdoors for some years without any treatment. The object is made of two parts. A round porthole and its round framework consisting mainly of grey cast iron. In the porthole broken pieces of the glass window are held in their original position in between the cast iron frame and a cast copper based alloy rim that are screwed together. A rubber isolating ring is located in a channel of the cast iron porthole, next to the rim. White paint is evident on the grey cast iron elements of the porthole under the powdery orange-brown crust and the copper based alloy rim is covered with a black paint. Both the porthole and its framework have two closing systems and a hinge. Parts of these closing systems are made of a copper based alloy. Figure 1 shows the front and rear of the porthole with all the different elements mentioned above.

a/ b/

Figure 1: General view of the porthole (a/ front side and b/ rear)

1.2 Condition report

When they were transferred to the conservation laboratory the two artefacts were covered with a very thin marine crust. The grey cast iron elements were heavily graphitized. The graphitization phenomenon corresponds to the corrosion of the metal that leaves behind a material that respects the original shape of the artefact but is made of iron corrosion products maintained together by graphite lamellas. Some fragments came off and many cracks were visible. The "weeping" phenomenon that is characteristic of active corrosion (Selwyn 1999) could be observed on the surface of iron based elements. The extent of the corrosion on some elements had provoked the breakage of the hinge and fastening systems. Abrasion in the marine environment further eroded the surface of artefacts. Copper based alloy elements in contact with iron elements were in a good condition due to the cathodic protection provided by the iron. The white paint covering some grey cast iron elements was loose due to past and current corrosion processes (during immersion in the sea and after exposure to the atmosphere). The rubber on the porthole was cracked due to its storage outdoors. UV-light, oxygen and ozone favour the deterioration of rubber (Lemaire 1993). The glass on the porthole was broken in its whole thickness. Only the edge was preserved. This condition survey clearly shows that the artefacts had suffered not only during their immersion of 40 years in the sea but after their recovery as well due to the exposure to new environmental conditions that accelerated further the alteration processes (North and MacLeod 1987, North 1987).

1.3 The research methodology

Both the porthole and its framework are composite materials that cannot be dismantled without damage. These artefacts had then to be treated as a whole. Due to their long exposure to the marine environment and the sensitivity of iron artefacts to chlorides we suspected the presence of aggressive chloride species within their structure. The observation of the “weeping” phenomenon on the surface of the grey cast iron confirmed this hypothesis. Exposing the porthole and its framework to a humidity chamber could be used to check whether these chlorides were active but since the risk of further damage was very high we decided to perform stabilisation treatment immediately.

Simple immersion of the artefacts can be used to extract aggressive chloride species, however, electrolytic processes are much more efficient (Degrigny & Lacoudre 1999). This is particularly interesting in the case of composite artefacts where associated materials such as glass, rubber and paint might get damaged during the process. Basic electrolytic equipments (power supplies, voltmeters and reference electrodes) available in the marine conservation laboratory at EVTEK, Institute of Art and Design were considered. Alkaline solutions (pH>9) used commonly to stabilise iron based materials could not be considered since the silica network of the glass may be damaged (Newton 1997), and paint layers are very sensitive to high pH. A neutral and safe solution for the associated materials had to be considered. The use of a buffer is a common practice to maintain a stable pH. Since we wanted to prevent any electrochemical activity that we would not be able to control we decided to use a non-buffered solution, with a chemical that had a minimal electrochemical activity. A preliminary study was needed to see how the system would react with time while applying a cathodic potential to the object in the selected neutral solution .

2. Experimental conditions

The treatment parameters were first determined using sacrificial coupons. Historic wrought iron nails (19th–20th century) were used because their microstructure made of ferrite is much simpler than the one of grey cast iron. To study the effect of different surface conditions on the electrolytic parameters the nails were either completely stripped of corrosion products (“bare” nails thoroughly polished), slightly cleaned (“slightly polished” nails where the powdery corrosion products were removed by polishing, leaving behind the magnetite (Fe_3O_4) layer), or left untouched (“corroded” nails presenting a double layer of red-brown and powdery oxyhydroxide ($FeO(OH)$) and black magnetite). No metallographic study of the nails was performed since historic wrought nails are usually made of ferrite and the amount of slag inclusions is rather low.

The nails were connected to the negative terminal of a power supply (Mascot, type 719) while a 316 stainless steel grid anode was connected to the positive terminal. A 1% (w/v) $NaNO_3$ neutral solution (pH=6.5-7) was chosen as an electrolyte because it is not active electrochemically in the range of potentials between the hydrogen bubbling on the cathode and oxygen bubbling on the anode. Furthermore, it should not have any effect on the associated materials. We tried in each experiment to expose a similar metal surface to the volume of solution considered (300ml). Velleman DVM 92 multimeters and an Ag-AgCl

Metrohm reference electrode (200 mV/SHE) were used to measure cathodic and anodic potentials and an Ecoscan pH-electrode to measure the pH.

Each experiment started by the monitoring of E_{corr} of iron nails in the $NaNO_3$ solution. Once E_{corr} value was stable the polarization could start. The surface of the nails changed during polarization and the “bare” and “slightly polished” nails had to be re-polished before each new experiment to recover the original appearance and obtain reproducible conditions. The “corroded” nails were only used once. Stainless steel anodes were cleaned before each polarization by immersion of a few hours in a 7% (v/v) HNO_3 solution.

Both the anodic and cathodic potentials were measured during the polarization and monitored with time. The monitoring of the anodic potential is rather unusual but since the stainless steel was systematically cleaned after each experiment we could use it as a reference material compared to the cathode that presented a different surface in each case. Measurements of the anodic and cathodic potentials were performed before measuring the pH. When using a non-buffered solution, stirring is needed to have a correct pH value but stirring modifies cathodic and anodic readings and when performed manually makes their monitoring with time rather difficult.

Experiments were performed on a 24 hour basis. This long period was chosen to simulate the treatment of real artefacts when treatment would proceed during days (where intervention is possible) and nights (where no intervention is possible). When an increase of pH was noted diluted HNO_3 (3.5 or 7% (v/v)) drops were added to recover a neutral pH. Therefore only the concentration of nitrates was increased. When a decrease of pH was measured diluted NaOH (10% (w/v)) drops were added increasing the concentration of the non active sodium cation.

Once the influence of the electrolytic parameters was better understood we could start the electrolytic stabilisation of the porthole and its framework and monitor the same electrolytic parameters as before with time.

3. Results

3.1 Simple immersion of iron coupons in neutral solution

Figure 2 shows E_{corr} measurements for all wrought iron nails whatever the surface preparation. The decrease of E_{corr} versus time occurs systematically and indicates the corrosion of the “bare” metal combined (or not) with the transformation of the corrosion layers (“slightly polished” or “corroded” nails). This experiment clearly shows that without any cathodic polarization iron artefacts, with or without corrosion layers, do corrode in a neutral 1% (w/v) $NaNO_3$ solution.

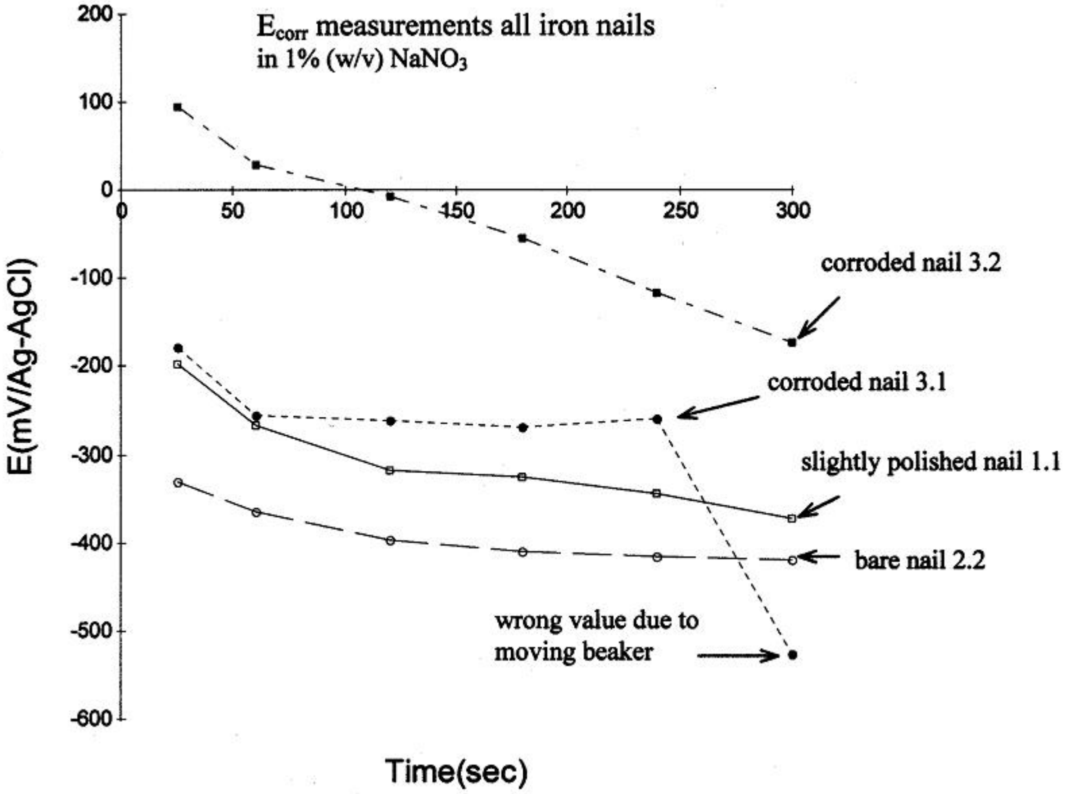


Figure 2: E_{corr} monitoring for "bare", "slightly polished" and "corroded" iron nails in 1% (w/v) $NaNO_3$ solution

"Corroded" nails have the higher initial potentials due to the presence of a thick corrosion layer that passivates the surface. The potentials obtained after five minutes of immersion (0 to -250 mV/SHE, Standard Hydrogen Electrode=0V) and inserted in a simplified Pourbaix diagram for Fe, confirm that in the present conditions the coupons should corrode (Figure 3). The stabilisation of iron based materials in neutral solution requires cathodic polarization to work.

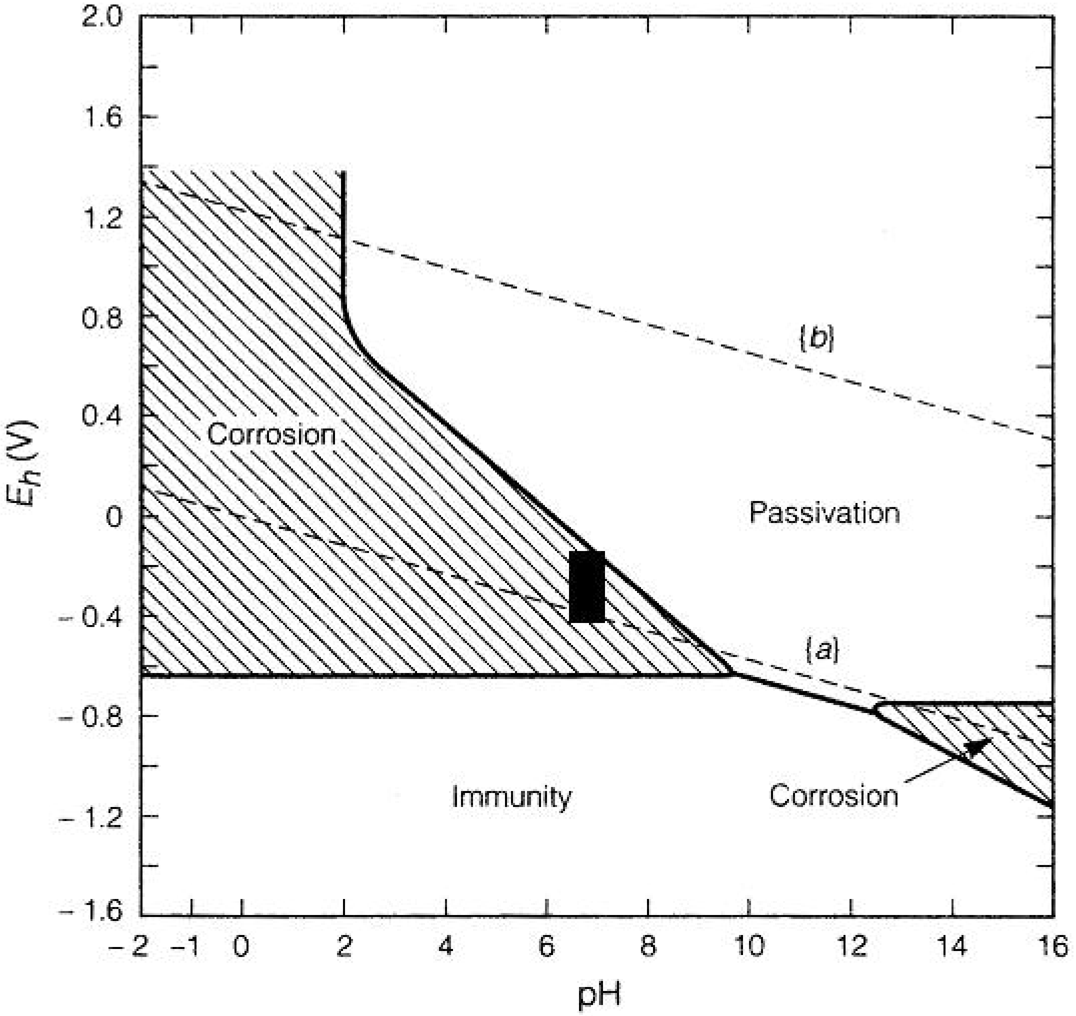


Figure 3: Simplified Pourbaix diagram for iron (concentration of Fe species ($<10^{-6}$ M)) (from Pourbaix 1963). The black area corresponds to the E_{corr} values for “bare”, “slightly polished” and “corroded” iron nails after five minutes of immersion in a neutral 1% (w/v) $NaNO_3$ solution

3.2 Polarization on artificial coupons

Polarization was started on “bare” nails at a cathodic potential of –1000 $mV_{/Ag-Ag/Cl}$ ($E_{Ag-AgCl}$=0.2V/SHE) (Figure 4). This potential is close to the one used for the treatment of another composite artefact in a neutral KNO_3 solution (Degrigny 2001).

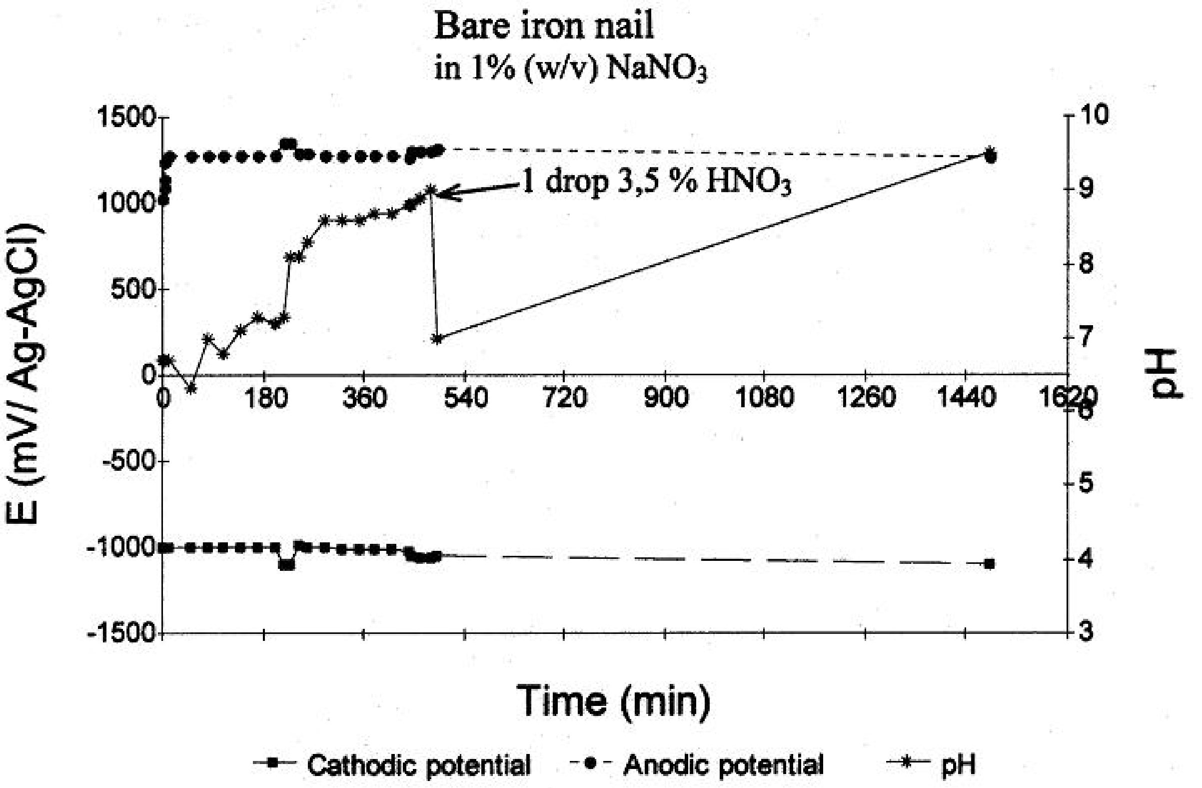


Figure4: Polarization of a “bare” iron nail at –1000 mV/$_{\text{Ag-AgCl}}$ in 1% (w/v) NaNO$_3$ solution. A drop of HNO$_3$ 3.5%(v/v) is added after eight hours. No modification of the solution could be performed afterwards (night)

Values indicated in Figure 4 are average values (around 1300 mV/$_{\text{Ag-AgCl}}$ at the anode). The pH increases slowly but constantly during the first three hours of the experiment. During two short periods while applying a more negative cathodic potential of –1100 mV$_{\text{/Ag-AgCl}}$ (after 215 minutes) and –1050 mV$_{\text{/Ag-AgCl}}$ (after 445 minutes) the pH increased faster than during polarization at –1000 mV$_{\text{/Ag-Ag/Cl}}$. A decrease in the cathodic potential has a direct influence on the anodic potential (immediate increase). Because the pH had increased to 9.0 after eight hours a drop of HNO$_3$ (3.5% (v/v)) was added to recover a neutral pH of 7.0. During the night when the system cannot be modified and drops cannot be added the pH increased again and the next morning a pH of 9.5 was measured.

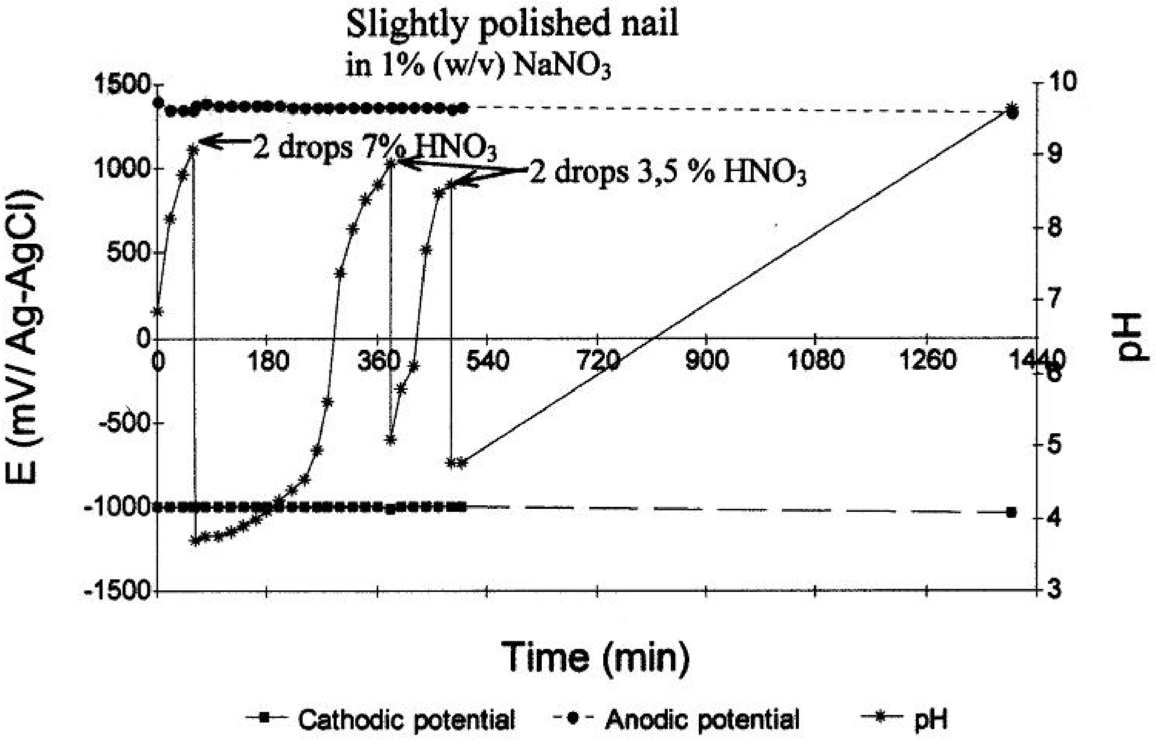


Figure 5: Polarization of a “slightly polished” iron nail at –1000 mV/$_{\text{Ag-AgCl}}$ in 1% (w/v) $NaNO_3$ solution

When moving from the “bare” nails to the “slightly polished” ones, similar results were obtained although the increase of pH was much faster (Figure 5). Drops of HNO_3 (even more concentrated than before) had to be added three times in eight hours to recover a neutral pH. Although the cathodic potential is the same as in the previous experiment the anodic potential was a bit higher, around +1400 mV$_{\text{/Ag-AgCl}}$. The application of a lower cathodic potential (around –800-900 mV$_{\text{/Ag-AgCl}}$) tended to slow down the increase of pH as indicated on Figure 6 but the extraction of chlorides is then less effective. Another way to monitor the treatment was by applying a constant anodic potential. This approach seems to be much more reliable practically, since the stainless steel is clean of any corrosion product and the surface is reproducible from one experiment to another.

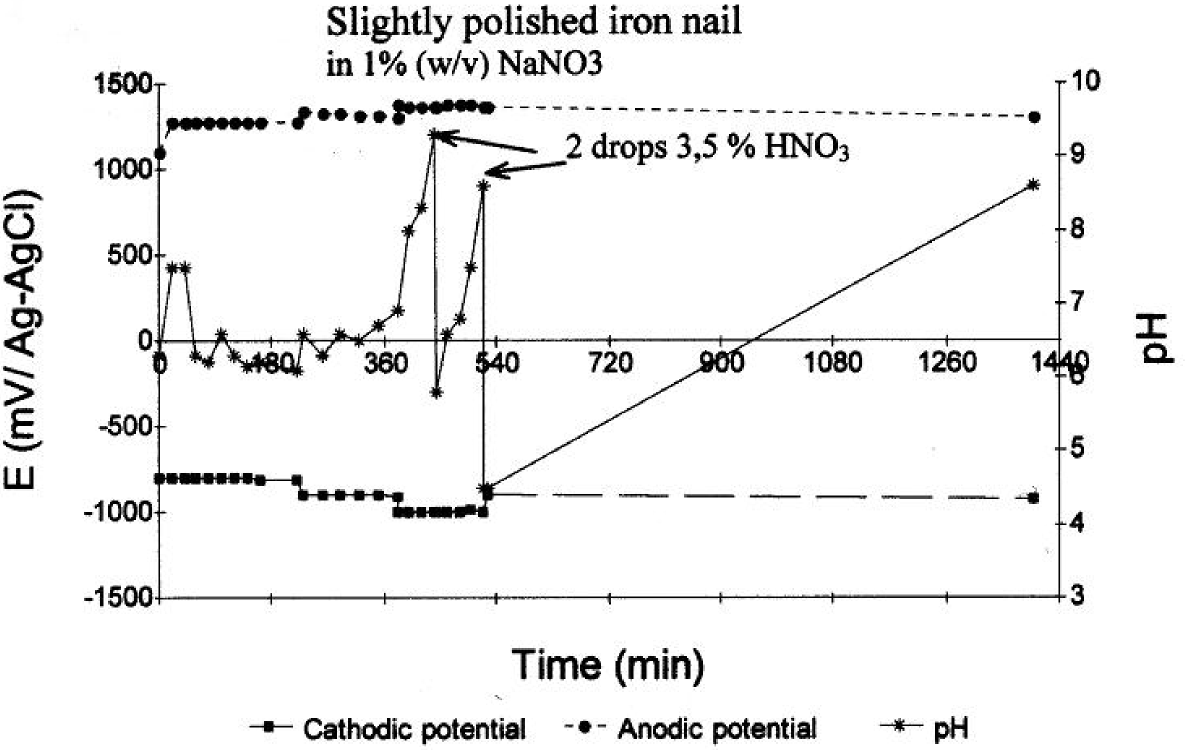


Figure 6: Polarization at different cathodic potentials and effect on the pH values in 1% (w/v) $NaNO_3$ solution

Based on the previous observation, preliminary experiments on the "corroded" nails were performed at –850 $mV_{/Ag\text{-}AgCl}$ (Figure 7). The anodic potential increased during the day from +695 $mV_{/Ag\text{-}AgCl}$ to +1000 $mV_{/Ag\text{-}AgCl}$. This value is much less positive than the one obtained with a "slightly polished" nail (Figures 4 and 5). There was no modification of pH during the first day and night. The cathodic potential was then decreased until bubbling of Hydrogen could be observed (-1465 $mV_{/Ag\text{-}AgCl}$). Hydrogen bubbling can damage the object and must always be avoided. At that value the anodic potential was around +1300 $mV/_{Ag\text{-}AgCl}$. By decreasing the cathodic potential back to –1100 $mV_{/Ag\text{-}AgCl}$ (anodic potential of 1200 $mV/_{Ag\text{-}AgCl}$) the pH remained stable. A stable pH at this cathodic potential was not observed with the "bare" and "slightly polished" nails.

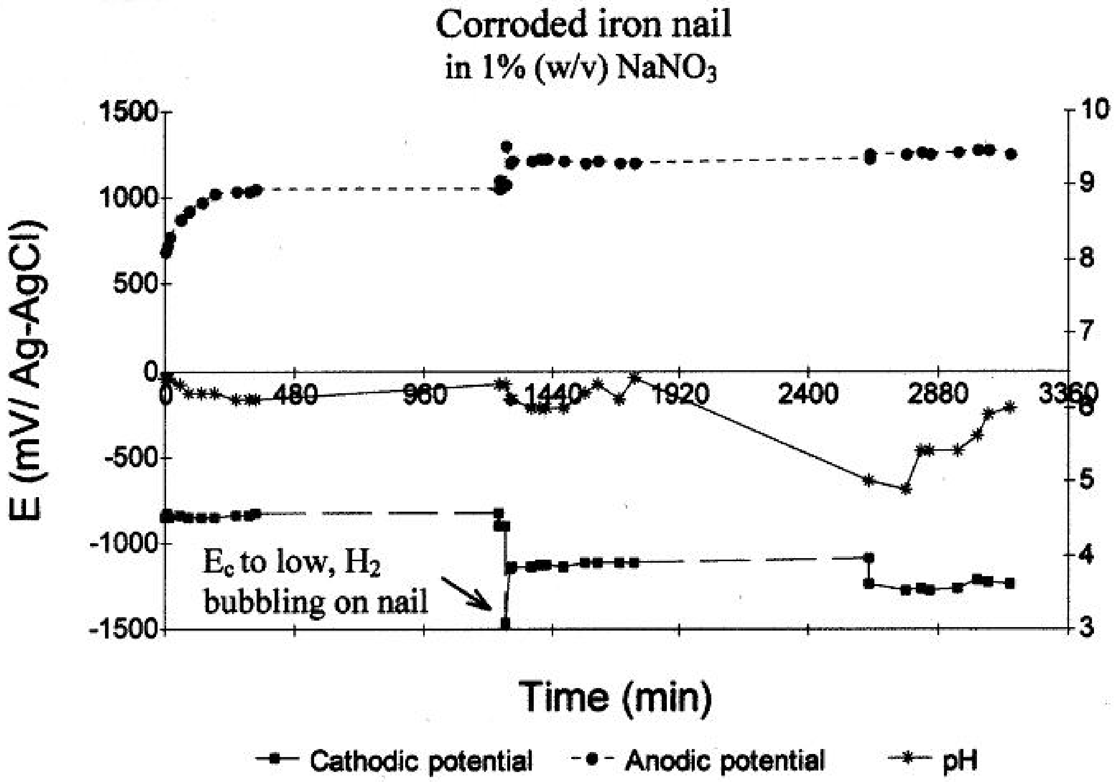


Figure 7: Polarization of a "corroded" iron nail at –850 mV/$_{\text{Ag-AgCl}}$ in 1% (w/v) $NaNO_3$ solution and effect of a modification of the cathodic potential on the other electrolytic parameters

The experiment was left for another night during which the pH decreased from 6.4 to 5.0. The decrease of pH can be as dangerous for the object as the increase of pH. The next morning the anodic potential was increased from +1200 mV$_{\text{/Ag-AgCl}}$ to +1250 mV$_{\text{/Ag-AgCl}}$. As expected from the previous experiments the pH increased slowly during the day from 5.0 to pH 6.0. The cathodic potential was around –1200 mV$_{\text{/Ag-AgCl.}}$

As a conclusion from these preliminary tests, the "corroded" nail reacted differently than the "bare" and the "slightly polished" iron nails. With the "bare" and "slightly polished" nails the pH increased when decreasing the cathodic potential below a certain value (around –800-850 mV$_{\text{/Ag-AgCl}}$).With the "corroded" nail a decrease of pH was observed in the same range of potentials (at least down to –1100 mV$_{\text{/Ag-AgCl}}$) The use of a non-buffered solution implies the requirement of constant correction of the pH either with drops of diluted HNO_3 or NaOH solutions. During the night when the system cannot be modified a less negative cathodic potential (and as a consequence a less positive anodic potential) should be applied to maintain the pH constant, or at least limit its modification. Finally the monitoring of the polarization through the anodic potential appears as an interesting approach when dealing with corroded artefacts.

Without plotting voltammetric curves (I=f(E)) both on the nails and the stainless steel it is difficult to tell which electrochemical reactions are really occurring when the potential of the nails is decreased or the potential of the stainless steel grid increased, and to find an explanation for the modification of pH. Hypothesis might be made as regards the reactions that are favoured. For "bare" and "slightly polished" nails the reduction of oxygen

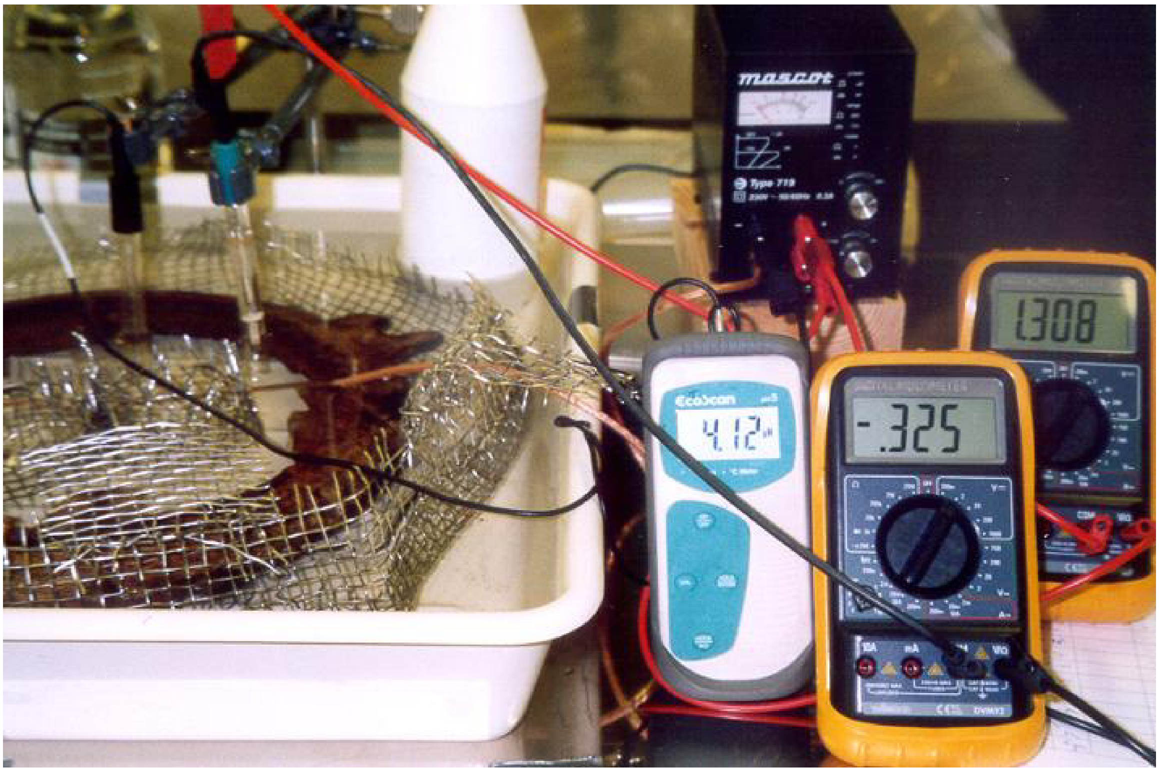
dissolved in the solution ($2H_2O+O_{2d}+4e^- \rightarrow 4OH^-$) accompanied by the reduction of oxyhydroxide and
Oxide layers ($3FeO(OH)+e^- \rightarrow Fe_3O_4+H_2O+OH^-$ and $Fe_3O_4+4H_2O+8e^- \rightarrow 3Fe+8OH^-$) are obviously favoured and this is reflected by the pH increase. Further investigation are required to find a reason for the decrease of pH when corroded nails are polarized.

3.3 Stabilisation of the porthole and its framework

Since similar stabilisation treatments were applied on the two artefacts only the porthole will be described in the following.

The treatment started by a mechanical cleaning of the corrosion layers on the grey cast iron elements. The objective was to remove any physical barrier to the extraction of chloride species. It was performed both with a scalpel and a hand held rotary drill with a soft abrasive wheel. Powdery oxyhydroxides layers could be removed but attention was paid not to damage the remaining, but loose, white paint covering the graphitized surface of the grey cast iron elements. No consolidation of the paint was performed at that stage.

Due to the extensive corrosion of the cast iron elements the electrical contact was made on the copper based rim. The wire was attached on a pre-polished area with “Araldite” rapid set epoxy adhesive. Stainless steel grids were placed in and outside the porthole. Through a bridge a good connection was made between the inner and the outside anode. The object together with the anode were placed in a plastic tank. To limit the volume of electrolyte to the minimum (to be able to better follow up the extraction of chlorides) spare containers were placed in the tank. The porthole was connected to the negative (-) terminal of the power supply and the stainless steel anode to the positive (+) terminal. The 1% (w/v) $NaNO_3$ solution was prepared with deionised water and to avoid its evaporation and pollution a plastic sheet covered the tank. The pH of the electrolyte at the beginning of the stabilisation treatment was 6.2 (the device is shown in Figure 8).



a/ monitoring of the electrolytic parameters

b/ covering of the tank with a polyethene sheet. Note the presence of spare containers in the tank to limit to the minimum the volume of the electrolyte

Figure 8: General device for the cathodic polarization of the porthole.

Based on the results obtained with "corroded nails", an anodic potential value of +1300 $mV_{/Ag\text{-}AgCl}$ was applied at the anode (Figure 9). The cathodic potential measured on the porthole was less negative than with the iron nail experiments: -300$mV_{/Ag\text{-}AgCl}$. The penetration of the solution within the graphitic corrosion layer expelled air bubbles that were trapped on the metal surface. These were not hydrogen bubbles since the applied cathodic potential was too low. The pH decreased very fast, in one hour from 6.2 to 4.8. No increase of pH could be obtained by increasing the anodic potential (to +1400 $mV_{/Ag\text{-}AgCl}$). The contrary happened: the pH became even lower; it decreased from 4.8 to 4.1. So the anodic potential was left at +1300 $mV_{/Ag\text{-}AgCl}$. The next morning the pH was 4.0 and the cathodic potential was –371 $mV_{/Ag\text{-}AgCl}$. In order to speed up the chloride extraction, the anodic potential was once again increased to +1400 $mV_{/Ag\text{-}AgCl}$ but both the cathodic potential and the pH decreased, the latter from 4.0 to 3.6.

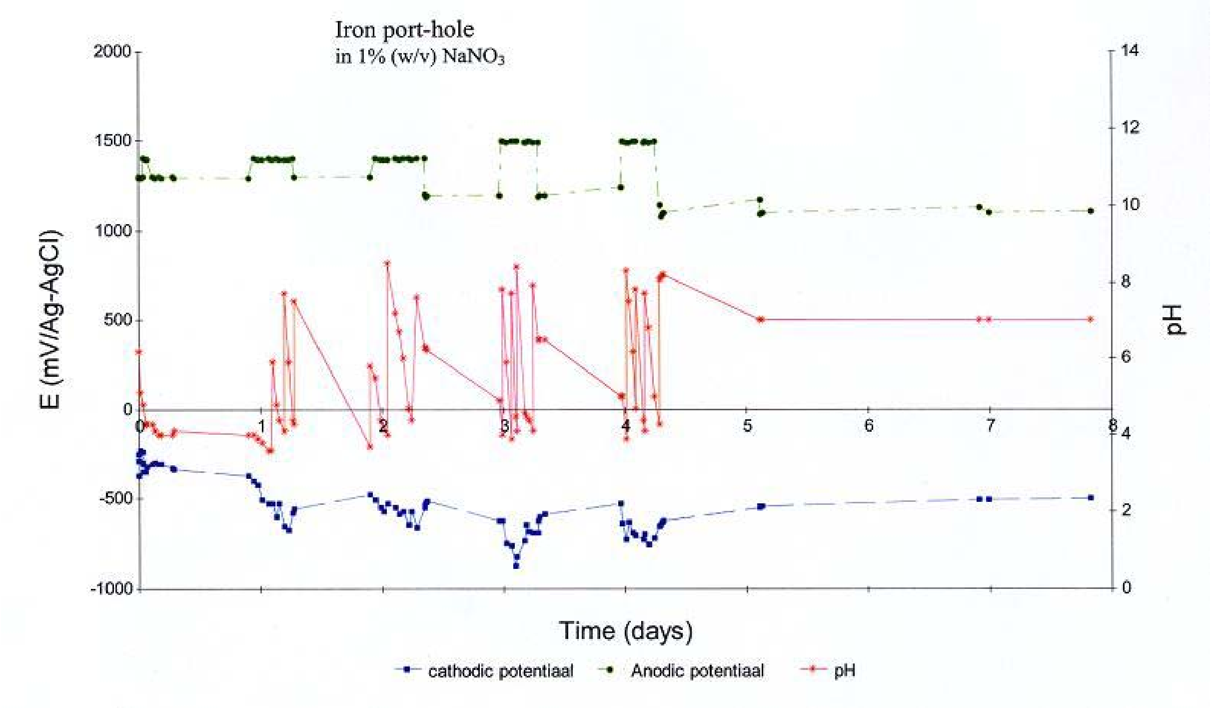
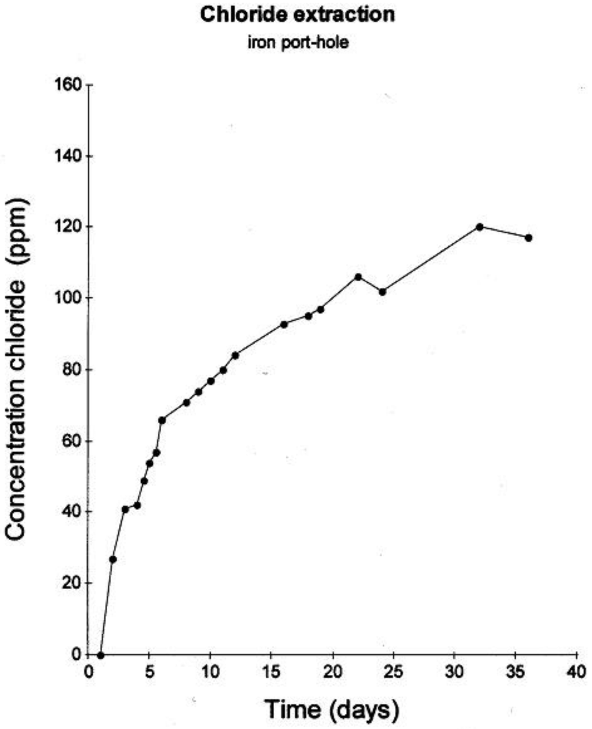


Figure 9: Monitoring of the electrolytic parameters during the cathodic polarization of the porthole in neutral $NaNO_3$ solution.. Drops of NaOH were constantly added during days 2, 3, 4 and 5 to maintain a constant neutral pH

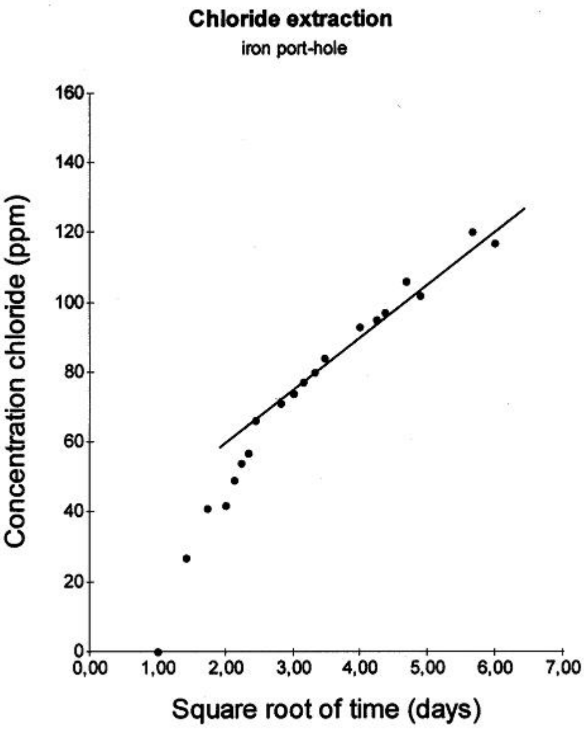
The solution had turned yellow due to the corrosion of the stainless steel, and iron species formed deposits at the bottom of the tank. Some also formed on the artefact but could be easily brushed away. Three millilitres of diluted NaOH solution (10%) was added to increase the pH from 3.6 to 5.9. Stirring is very important while adding NaOH to obtain an equal pH for the whole electrolyte. The process of adding NaOH was repeated every two hours during the day. The volume of NaOH that was needed to get a higher pH was different each time. Before we left the object during the night we decreased the anodic potential to +1300 $mV_{/Ag-AgCl}$.

The process of increasing the anodic potential to a more positive value during the day, decreasing the anodic potential to a less positive value during the night and controlling the pH by adding a few millilitres of NaOH was repeated during the next five days. Since the increase of the anodic potential did not increase the pH it was decided to decrease the anodic potential to see how the pH would react. The first two nights an anodic potential of +1300 $mV_{/Ag-AgCl}$ was applied. The third and the fourth night an anodic potential of +1200 $mV_{/Ag-AgCl.}$ During the fifth night an anodic potential of +1100 $mV_{/Ag-AgCl}$ was applied and a stable pH was finally obtained.

Adding a few millilitres of NaOH every two hours is time consuming and therefore not a realistic way to treat an artefact in a conservation laboratory. Also it is unknown whether this rapid fluctuation of pH (between 4 and 8) can damage the object as well. Therefore it was decided to continue the treatment at an anodic potential of +1100 $mV_{/Ag-AgCl}$ for which the cathodic potential measured on the porthole was –500 $mV_{/Ag-AgCl}$.



a/



b/

Figure 10: Monitoring of the extraction of chlorides versus time (days) (a/) and the square room of time (b/) for the porthole, under cathodic polarization in neutral $NaNO_3$ solution

During the treatment the extraction of chlorides was monitored. The extraction was faster during the first six days as can be seen in Figure 10a, when the applied cathodic potential was more negative. When plotting the values versus the square root of the time (Figure 10b) we realised that the values obtained were eventually on a straight line. The extraction of chlorides appears to be following a diffusion law.

Due to the sudden closure of the conservation laboratory, the treatment had unfortunately to be interrupted and we did not have the chance to follow up the end of the stabilisation process.

4. Conclusion

We have shown through this project that it is possible to stabilise a marine metal composite artefact constituted mainly of grey cast iron, in a neutral and non-buffered solution with basic electrolytic equipment: a power supply, a reference and pH electrodes, two voltmeters and a pH meter.

Preliminary experiments were performed on iron nails covered (or not) with corrosion layers, to determine the safest electrolytic parameters. The study of “corroded” nails was particularly interesting since we found out that their electrochemical behaviour is different from the one of “bare” or “slightly polished” nails.

While polarizing the highly graphitized porthole, we decided to work under constant anodic potential conditions and to monitor the cathodic potential measured on the artefact. Although the behaviour of the latter seemed to be similar to the one of “corroded” nails, we had to adapt the parameters in a way to protect the artefact (by maintaining a constant and neutral pH) but obtain too the most efficient extraction of chlorides.

The methodology followed has shown its limits. We now need to plot voltammetric curves to understand the electrochemical reactions involved during the polarization process. Still, we have now some ideas of the range of cathodic potentials that are suitable for such a treatment.

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Theophilus and the shrine of Vitus-
A goldsmith's technique in the mirror of ancient references

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Abstract

This investigation of a Romanesque reliquary dating about 1200 AD, is a comparative study of Theophilus´ treatise *On divers arts* and other treatises, and the methods used for manufacturing this shrine. Scientific analysis of the shrine's enamel and niello work reveal quantities of boron in the enamel, which are absent in the niello. A bibliographical survey documents acquaintance and use of borax in Greece, in the Arabic and European middle ages until today. The possible use of borax in niello and solder work in the time of the manufacturing of the shrine is presumed. According to present knowledge, two enamel sheets of the shrine can thereby dated to modern times.

Résumé

Cette étude d'une relique romane datée d'environ 1200 AD cherche à montrer le rapport entre les méthodes de production de l'orfèvrerie et les formules des sources techniques de la même époque, comme *De diversis artibus* de Theophilus Presbyter. Les analyses scientifiques de l'émail et de la nielle détectent des quantités marquées de bore dans l'émail, mais pas dans la nielle. Une étude des sources documente sur l'usage et sur la connaissance historique du bore. Le résultat est la datation de deux plaques émaillées aux temps modernes. Cette recherche démontre la possibilité de la datation par la détermination des quantités de bore, en cas échéant.

Keywords: borax, flux, enamel, niello, medieval goldsmith technique, Theophilus

1. Introduction

Reliquaries make up a significant part of collections of medieval sacred goldsmith's work. This research work deals with the so-called *Vitusschrein*, a Romanesque altar-shaped reliquary from the former Benedictine monastery Willebadessen near Paderborn (Westphalia, Germany). Investigation of the manufacturing methods offered the possibility to research a material, which often eludes scientific analysis: borax. The study is an enlarged part of a diploma dissertation at the State Academy of Art and Design in Stuttgart, Germany (Grieb 2004).

After a short description of the shrine, the study focuses on borax and deals with the manufacturing process of the shrine. Historic treatises are dealt with, which document the circumstances of trade and availability of borax in Europe and the usage as a flux in medieval metallurgy and goldsmith's work. Based on contemporary references, the reason for the confusion about this material in these times is analysed. Thereby, some myths surrounding this material will be unveiled.

2. Description of the shrine

This goldsmith's work is of special importance, because it was manufactured in an area near the monastery Helmarshausen, where the famous goldsmith Rogerus of Helmarshausen operated his workshop. Dendrochronological investigation as well as historical observation suggest a manufacturing date no more than 70 years after the time of Rogerus. The shrine of Vitus is dedicated to a monastery not far away from Paderborn, where the well-known reliquary of Kilian and Liborius is kept. It is maybe the most famous of Rogerus' works. In addition to this, the monk Theophilus Presbyter, author of the goldsmith's treatise *De diversis artibus*, seems to be identical with Rogerus. It can be suggested, that the goldsmith of the *Vitusschrein* was aware of this treatise and maybe used his recipes.

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Figure 1. The shrine of Vitus.

Figure 2. The lid of the shrine of Vitus.

The shrine is square-shaped with a lateral length of 28,8 cm, a width of 16 cm and a height of about 20 cm. The shape, which emphasizes the horizontal and vertical lines reminds us of an altar, but the shrine never had this function.

It is constructed of a case made of oak, sheathed with chased, gilded silver and copper sheets. The sheets are decorated with niello and enamel. Around the middle part (stipes), the twelve apostles are depicted; the lid shows Jesus Christ in the centre accompanied by the Holy Mary and the Holy Vitus. In the corners, the four evangelists can be seen.

Gilded copper sheets, which are decorated with enamelled inscriptions, cover all sides of the shrine. For the decoration, the technique of email champlevé was employed. Two sheets on the lid are decorated with tendril motives carried out in blue email champlevé.

Figure 3. The shrine's left enamelled sheet.

Figure 4. Detail of the nielloed sheet below the figure of Jesus.

The tops of the left sheet tendrils are decorated in turquoise colour. Two gilded sheets inscribed with prayers in niello complete the motive of Jesus Christ.
These nielloed sheets in combination with the two enamelled sheets of the lid are the major subjects of this study.

3. Analysis of the shrine

Scientific research on the shrine of Vitus focussed on gaining relevant information to help understand the manufacturing process and history of the shrine. It was of main interest to find evidence for the dating and the authenticity of separate constructional parts. Detailed analysis was carried out on the appliqués of the lid, particularly on the enamelled and the nielloed sheets, as later alteration or trimmings were suggested.
The crowded arrangement of the lids decoration is remarkable, as Figure 2 demonstrates. The surface of the enamel is not worked down to the level of the base metal as usual, but shows an untypical fire-glaze. This stands in contrast to the enamel of the shrines body. The decoration of the sheet metal as a background was carried out using a decoration technique (quaver engraving) which is completely untypical for medieval times. The arrangement of the two tendrils is also not characteristic for medieval times. Art- historical investigation suggests a product of the art noveau movement (Kötzsche in: Grieb 2004).

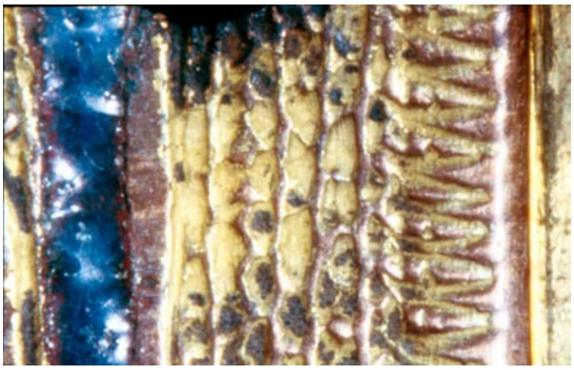
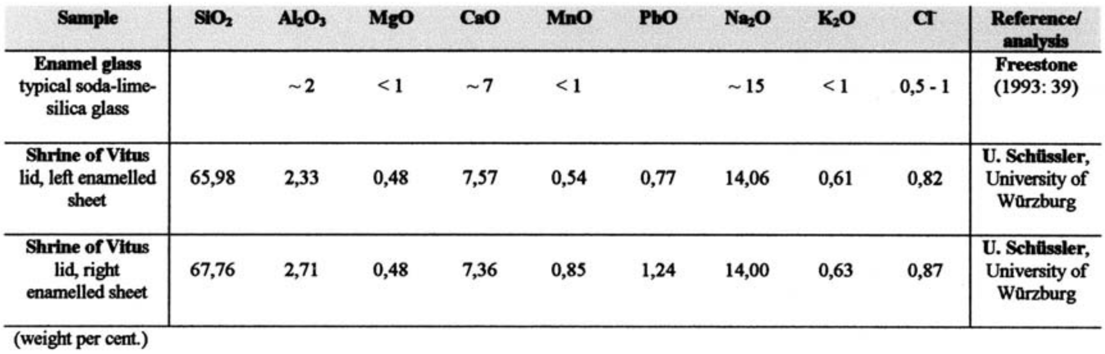


Figure 5. Detail of the right enamelled sheet.

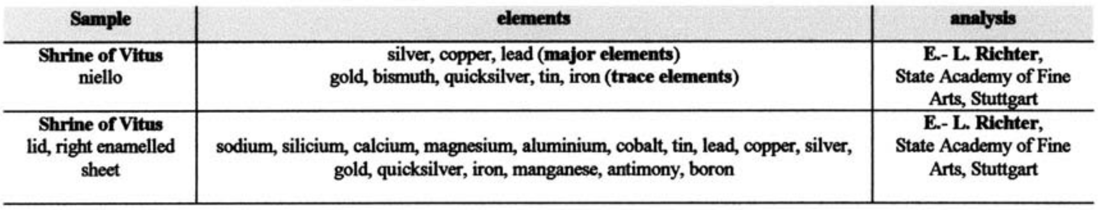
However, XFA-analysis of the enamels did not point to a modern work; the glass compounds were nearly corresponding with the typical Romanesque soda-lime-silica-composition defined by Freestone (1993) as demonstrated in Figure 6.



Sample	SiO_2	Al_2O_3	MgO	CaO	MnO	PbO	Na_2O	K_2O	Cl^-	Reference/ analysis
Enamel glass typical soda-lime-silica glass		~ 2	< 1	~ 7	< 1		~ 15	< 1	0,5 - 1	**Freestone** (1993: 39)
Shrine of Vitus lid, left enamelled sheet	65,98	2,33	0,48	7,57	0,54	0,77	14,06	0,61	0,82	**U. Schüssler,** University of Würzburg
Shrine of Vitus lid, right enamelled sheet	67,76	2,71	0,48	7,36	0,85	1,24	14,00	0,63	0,87	**U. Schüssler,** University of Würzburg

(weight per cent.)

Figure 6. Typical Romanesque enamel compound and selection of XRF-analysis of the lid’s two enamelled sheets.



Sample	elements	analysis
Shrine of Vitus niello	silver, copper, lead (**major elements**) gold, bismuth, quicksilver, tin, iron (**trace elements**)	**E.- L. Richter,** State Academy of Fine Arts, Stuttgart
Shrine of Vitus lid, right enamelled sheet	sodium, silicium, calcium, magnesium, aluminium, cobalt, tin, lead, copper, silver, gold, quicksilver, iron, manganese, antimony, boron	**E.- L. Richter,** State Academy of Fine Arts, Stuttgart

Figure 7 Emission spectroscopy analysis of the niello and the right enamel sheet’s glass.

Analysis carried out with Optical Emission Spectrography (OES), which is able to detect light elements, showed distinct amounts of boron. Boron is added to the molten glass in the form of its compounds; in former times, mainly borax was used. The analytical result is somewhat surprising, because Theophilus and other authors of that time did not mention any additives of this origin in the enamel glass.

Subsequently, an OES-analysis of the nielloed sheets was carried out, but no boron could be detected. If the goldsmith who made the shrine of Vitus followed Theophilus’ recipe, boron should have been present. Theophilus mentions the fusing of niello in his third book, chapter 29:

„*When you have filled several quills* [with the niello powder] *in this way, take the resin called borax and grind a small piece of it with water in the same pot, so that the water is rendered just turbid from it. Wet the place you want to cover with niello with this water first; next, take the quill and with a light iron rod tap out the ground niello carefully over the place until you have covered it all, and do the same everywhere. Then heap together well-burning coals and put the bowl into them, covering it carefully in such way that no coal is placed over the niello or can fall on it.”* (Hawthorne and Smith 1979).

Most editors translate the formulation “*...accipe gummi, quod vocatur parahas...*“, (named “*barabas*” in the manuscript of Wolfenbüttel) as “take the resin called borax” (discussed in: Grieb 2004).
In theory it should astonish us that the niello compound does not seem to contain boron. How can this discrepancy be interpreted? On the one hand, a significant content of boron was found in the enamel-glass, although not verified by Theophilus, alternatively there is a lack of boron in the niello, where he describes the use of borax. To clarify this question it appears necessary to look into the matter of borax.

4.1 What is borax used for? –General remarks on the use of borax as a flux

Borax, named chemically as sodium tetraborate decahydrate, is used in goldsmith work in the form of the pentahydrate, called “jewellery borax“. Because of its good ability to dissolve metal oxides, it is used in many high-temperature processes, such as soldering, refining metals, or in nielloeing where obstructing

interfering metal oxides have to be removed. On the one hand borax dissolves metal oxides and removes them from the work piece, but also, it forms a glassy coating which prevents the reaction with oxygen.
Borax, in the form of boron oxide, has another function as a component in glass used for enamel inlays. Boron oxide acts as a network former and as a flux. The term "flux" in glass technology, means an alkaline compound which lowers the melting temperature range of a glass. It raises gloss and physical stability, lowers the fusion's viscosity in high temperature ranges, and most important of all it lowers thermal expansion. (Petzold and Pöschmann 1987).

4.2 Where is it mined? – Origin and production

Borax occurs naturally in a mineral form called "tinkal". It appears in transparent or white, sometimes bluish, greyish or greenish crystals, which are astringent and have a slightly sweet taste. Sites of discovery are the shallow zones of hot springs, and the mud of so-called borax lakes in western Tibet and Cashmere. Borax is found together with Glauber's Salt, rock-salt, gypsum, soda and other minerals. Tibet is commonly known as the source of borax in medieval times. Discoveries of the fumaroles sites in Tuscany near Siena as well as in Turkey, and the extensive discoveries in North America are prospections of the 19th century.

The mineral tinkal, respectively the tinkal soaked earth is refined, and the borax is extracted. Georgius Agricola demonstrates the steps of this refining process on a copper engraving included in his work *De re metallica*.

Figure 8 Refining borax referring to Georgius Agricola.

He refers to the refining of soda, but he confuses it with borax, which he calls chrysokolla. Illustrated is the preparation of the aqueous solution in a vat (A), the boiling and concentration to a supersaturated hot solution in a rectangular pan made from copper (B), the crystallising in a second vat (C), where copper rods are used to support crystallization (D) and the crushing of the crystals in a mortar (E) (Schiffner 1977; see Figure 8)
Most of the borax was traded not in the crushed powdery form, but crystallized, sometimes packed in wooden caskets mixed with animal fat. This way, it reached as far away as Venice.

4.3 Since when is borax known? – Borax in ancient Greek and Arabic sources

As legend has it, the Babylonians and Egyptians used borax four thousand years ago in metallurgy, mummification and medicine. Craftsmen of ancient China used borax in ceramic glazes. First written reference can be found in the Indian text *Arthasastra*, about 300 B.C., "*Borax, which goldsmiths use for welding"* (Wolters 2001).

Unfortunately none of the Greek writers like Theophrastus, Galen or Zosimos mention borax. Only Dioscorides and Pliny the Elder refer to chrysokolla, a "*gold-glue*", which seems to be a mixture of copper ores. In later times, chrysokolla is often confused with borax, because like borax it is used for soldering, and it is an important ingredient for reaction soldering. First reference of borax in ancient Greek times is found in manuscripts of the Late Greek period of the 7th century A.D.

It is assumed that areas north of the Alps had no knowledge of this material in these early times. But it should be kept in mind, that it is not impossible to suggest use of borax in Roman, Carolingian or Viking techniques. However, there is a have a lack of evidence until the present day. Through contact with the Arabic world during the Christian crusades, and particularly during the occupation of Spain, the Occident came in touch with the profound knowledge of alchemist, astrological and medical matters, and its Greek sources. A study dealing with borax should take a glance at the tractates of the Arabic scholars.

The Islamic chemist Jabir ibn Hayyan (Geber arabicus, 8th c.) mentions *Boraces* as an independent class of minerals next to salts, alums, vitriols and others, but little can be learnt about sources or use. The first definitive reference is found in the works of the Persian physician Al Razi (born and died in Ray, Iran, 865-925). He classified substances into animal, vegetable and mineral matters and subdivided minerals into six categories: Spirits (which sublimate when heated), Bodies (like the metals gold, silver, tin, iron or lead), Stones (like Malachite, pyrites, glass), Salts (rock-salt, potash and other wood ashes), Vitriols (green, yellow, white vitriols) and Boraces (Haage, 2000).

A Coptic Papyrus found at Meshaikh, dating around the 10th century A. D., documents medical prescriptions. It mentions Armenian borax (*"paurak armenei"*) (Travis and Cocks 1984).

Al Hamdani, 942 A.D in Yemen, refers to *burnt tinkar* for purifying gold and silver as well as for soldering, in his work *Kitab al jawharatain al atiquatain* (The precious metals gold and silver). For use in nielloeing he writes *"If they want to inlay (?) silver with this (the niello-compound), they pound it up with borax (tinkar) and water, and fill the place dug out of the silver with this pulverised material. It is allowed to flow like solder in the oven, and it does so."*. Ibn Hawqal (about 978 A.D.) reports on goldsmith's borax from Lake Urmiya (Aserbaidschan), which was used as a flux. He comments: "*it makes substances flow*" (Allan 1979).

Mainly in Spain, Arabic alchemist knowledge was unveiled to European scholars. Results of this interchange of ideas are Arabic scientific works, which became translated into Latin, e.g. *De aluminibus et salibus* (Of alums and salts written by Pseudo-Rhazes). In this document, borates are no longer a class of minerals on their own, but borax is called a salt. The *Liber Sacerdotum* of the 10th century which mentions borax is also a translation of an Arabic text.

4.4 Borax in European references – Soldering and Nielloeing

Not only technical knowledge, but also the material borax itself reached Europe. It is supposed that borax was brought from Mongolia to Venice by Marco Polo in 1295, but borax is mentioned in texts north of the Alps much earlier, which indicates that usage of the material might be possible before the 13th century. A 12th century recipe of the *Mappae Clavicula* deals with borax used for nielloeing: "*Afterwards temper some atincar [...] with water, and with this temper the niello and place it where you wish [...]. Sprinkle soda [natronum] powder on top, and put it on coals until the niello runs well.*" (Smith and Hawthorne 1974). Theophilus' reference is mentioned above. Heraclius writes, "*...and then take the liquor which is called borax...*" (*accipias illum liquorum qui vocatur bures*) (Merrifield 1967).

Later on, borax is quite frequently mentioned, often in connection with preparing niello. The manuscript of Montpellier 1430 reports: "*Take lead, copper as well as silver und fuse the same quantity. Is this done stir with a red-hot charcoal, add sulphur, as much as the amount of the three metals and stir with a red-hot charcoal. Fuse the sulphur and when it is burnt out, pour the mixture to where is clear water, temper with Borax and paint any ornament" ("...et cum boraxa distempera...*". "*Nimm Blei, Kupfer ebenso Silber und schmilz es zu gleichen Teilen. Ist das geschehen, rühre mit einer glühenden Kohle um, nachher füge Schwefel hinzu, soviel als die drei Metalle an Menge ausmachen und rühre mit einer glühenden Kohle um. Schmelze den Schwefel und wenn er ausgebrannt ist, gieße das Gemenge dahin, wo klares Wasser ist, mische mit Borax und male beliebige Schnörkel.*" Rosenberg 1972). Biringuccio 1540 describes borax: "*Borax is of two kinds, natural and artificial. Natural borax is a clear fusible stone of a form like that of sugar candy or rock salt, although Pliny says that it was green, and that it served not only to solder gold but also for painting. It is mined today in Germany. It is easily crushed and pulverized. Artificial borax is made of rock alum and sal ammoniac. Both kinds have the property of facilitating the melting of metals, and they unite and solder whatever they are put on.*" (Smith and Gnudi 1990). 1568 Cellini recommends the use of "*well ground borax from the dredger*" for soldering silver and for soldering with verdigris (Wolters 1986). As well, he uses it in nielloeing: *"Pour your niello which consists of many grains now again in a crucible and it melt in adequate fire with a grain of borax. [...] Is this done spread it over the plate, which you engraved, using a spatula made of brass or copper, evenly covering the plate in the height of the back of a knife. Spread a little well ground borax over it, but not too much, [...]"* (*Schütte sodann deinen Niello, der jetzt aus vielen Körnern bestehen wird, aufs neue in den Tiegel und lass ihn bei passendem Feuer mit einem Körnchen Borax schmelzen. [...] Ist dies geschehen, so breite ihn [den Niello] mit einer Spatel von Messing oder Kupfer über die Platte aus, in welche du eingegraben hast, und zwar so, dass es sie in der Höhe eines Messerrückens gleichmäßig bedeckt. Nun streue etwas gut gestossenen Borax darüber, aber ja nicht zu viel, [...]* Brinckmann 1978).

After the 16th century, borax vanishes in nielloeing and is replaced by other fluxes like saltpetre, sal ammonic and several mixtures. But in fluxes for fusing and soldering it is still an important ingredient until today. For example, Tomasco Garzoni writes in 1580: *"When it happens that they have to solder, so they do it with low silver or burnt copper with borax…*" (*Wann es sich zutregt/ daß sie auch Löten müssen/ so thun sie* *dasselbige entweder mit geringem Silber/ oder gebranntem Kupffer un Borax…* Wolters 1986). Last reference is the goldsmith's treatise *Der künstliche Gold- und Silberarbeiter* from 1708: *"Soldering broken florins. Take ground verdigris, wet put in on the chink, then pour borax on top, let it become red-hot on glow, so the borax will melt and solder together the florin."* (*Zerbrochene Gülden zu löthen. Nimm zerriebenen Grünspan, lege es nass auf den Ritz, dann schütte Borax darauf/ laß auf einer Glut solchen zerglüen/ so zergehet der Borax/ und löthet den Gulden wieder zusammen.* Wolters 1986).

4.5 Borax in European references – Enamelling

In Europe, boron as a compound of enamel glass appears in more recent times, approximately in the 17th century. It is added to the glass compound as a flux in the form of borax. The positive effect of borax for enamelling is first mentioned by Robert Dossie in *Handmaid to the Arts* from 1758. Older references, such as J. G. Kunckel, A. Neri or De Blancourt, do not mention borax in connection with enamel. A manuscript from either De Mayerne, or the enamellist Jean Petitot dating before 1640, mentions "*buros*" or "*bouros*", which is probably borax (Speel and Bronk 2001). Only in the 19th century, borax was more widely used as an enamel component, facilitated by the better availability, the lower price and the upcoming technology of enamelled iron.

4.6 How did borax reach Europe? Trade and trouble

The borax trade to Europe was via Venice for a long time. Scientists and Craftsmen of Venice knew about the secrets of raffination and guarded it with distrust. Thereby, Venice held the monopoly for a long time and regulated price development by forcing it to a staggering height. The Venetian Borax, "Borax veneta" or "Borrax raffiné", used to be extremely rare in Europe; it was expensive and therefore unattainable and desirable. Johannes Kunckel (1679) deals with this fact when describing a glass mixture by eulogizing borax: "Following composition is much more precious, but equally all the more beautiful…" (*Nachfolgende Composition ist zwar kostbarer, aber auch um so viel desto schöner…* Kunckel 1992). A great quantity of surrogates were invented to replace the desirable material. At the end of the 17th century, the Dutch gained knowledge of the secret of raffination, took over the trade monopoly and held it for almost one hundred years up to 1770, when the French conquered India and derived new tinkal sources. Due to these new sources, and deposits in the New World, the price declined during the 19th century, and borax was available for a broader industrial use.

5. What is meant? - Confusion of the references

When browsing through literature it must be kept in mind that the term borax was not only used to describe borates, but was used as a synonym for flux as well. In addition, several mixtures and surrogates are described. In earlier times it was difficult to differentiate between the different salts, which led to confusion. Mistakes of transcription and misunderstandings of the writers, often because their sources of technical information misled them, caused confusion for hundreds of years.

5.1 Poor Descriptions

Even the initial term, 'borax', was not exact. The medieval translators of the Arabic alchemy texts use the Latin term *borax* variously for a whole group of terms like Hebrew *borith*, Arab *baurach* or *paurak,* Persian *boreck* or Turk *burack,* as well as *bora, baracha burah* or *burraq*. These terms all mean the same: shine, glint, twinkle. It is the description of the appearance of a material, and it does not necessarily refer to borax. The categorization of minerals developed by the physician and philosopher Al Razi (865-925) lists the following under the sub-class of borates: *Tinchar* (*tinkar*), *goldsmith's borax*, *bread borax*, *natron*, *borax of Zarawand* and *buraq al garb*. These listing shows how broad the meaning of the term used to be. *Natron* normally denotes impure natural soda (Latin *nitrum*, *natronum*, or *trona*, Arab *natrun*); it is a mixture of sodium carbonate and bicarbonate. Maybe *bread borax* meant bicarbonate as well. *Goldsmith's borax* might be borax or another borate (possibly the same substance referred to by al Hamdani and Ibn Hawqal), but he describes it as a white efflorescence like the saltpetre found on walls. *Borax of Zarawand* could be this substance as well. Kashani writes about *ranravandi* or *zarvandi*, the name of a village near Nishapur, in his opinion the place of origin. Other references mention a river in Armenia. *Tinchar* seems to be the product of a refined substance, made by boiling *buraq* with *a quail salt and* "*buffalo milk*". This is why Al Razi calls it artificial borax (Travis and Cocks 1984). Actually, the refining technique of borax requires the use of lime-wash (calcium hydroxide), and that probably misled Al Razi. *Tinchar* originates from the Sanskrit word *tincana* or *tankana,* meaning borax from Tibet and Cashmere. Interesting information is provided by the reference on *buraq al garb*, which is not a mineral substance, but the gum of the willow or acacia tree (the Arab word *algharab* stands for *willow*).

5.2 Mistakes in transcription

The confusion of the European writers, created by mixing up Arabic knowledge with Greek and Roman texts, was already present in the Arabic alchemy. The dictionary of Bar Bahlul of the 10th century mentions "*Chrysokolla, tankar, tanacarau; material, craftsmen use for soldering, tankar*" (Wolters 1986). The term *chrysokolla*, or *auricolla*, *capistrum auri*, *gluten auri* reaches back to the Greek scholars and describes *gold glue*, which is mainly copper oxide used for soldering by reduction, but no salt used as a flux. Confusion was even worse with European authors. The German Georgius Agricola was misled by the text of Pliny and by those who informed him. He confuses soda with chrysokolla and borax. In his text *De natura fossilium* he writes in 1546: *"Natural soda is prospected in the earth or outside of the earth. In the earth you find it hard, dense and more similar to a stone. Of this origin is soda, of which in Venice chrysokolla –as I call the borax- is made. […] The second form of artificial soda is produced of a mined soda even today – in Arabic it is called tinkar. I use to name it, as said before, correctly with the Greek term chrysokolla and not with the Arabic [term] borax."* (*Natürliche Soda findet sich in der Erde oder außerhalb der Erde. In der Erde findet man sie hart, dicht und mehr einem Stein ähnlich. Von dieser Art ist Soda, aus der man in Venedig die Chrysokolla – so nenne ich den Borax – herstellt […] Die zweite Art der künstlichen Soda wird noch heute aus einer Soda, die man bergmännisch gewinnt – arabisch heißt sie Tinkar – hergestellt. Die pflege ich, wie gesagt, mit Chrysokolla, wie es richtig ist, mit dem griechischen Worte zu bezeichnen, als Borax mit dem arabischen…* Wolters 1986).
As well he writes in *Epistola ad Meurerum* (1546) "*Chrysokolla ex nitro confecta Borras"*. His description in *De re metallica* (1556) is well known, which is illustrated by the copper plate of Figure 8: "*chrysokolla, which the Moors called borax"*.

In 1756, Dr. Samuel Johnson characterizes borax in his dictionary with the following words: "*Borax (Borax low Latin), an artificial salt prepared from sal-ammonic, nitre, calcined tartar, sea-salt and alum, dissolved in wine. It is principally used to solder metals and sometimes as an uterine ingredient in medicine.*" Ten years later, Pierre Macquer, professor of chemistry in Paris, has to admit in his Chemical Dictionary "*…We are far from knowing as much concerning borax as is desirable. We are even ignorant of its origin"* (Travis and Cocks 1984).
It took time up to 1808 until the element boron was discovered and the nature of borax was unveiled.

5.3 Surrogates

Apart from inexact or wrong description, several recipes for surrogates called "borax" exist. For example, Andreas Libavius writes in 1597: " The ingenuity of the goldsmith has created several chrysokolla for soldering gold and silver, which they call borax." (*Der Erfindungsgeist der Goldschmiede hat zum Löten von Gold und Silber allerlei Chrysokolla erfunden, die sie als Borax bezeichnen*, Wolters 1986).
J. G. Krünitz (1788) reports of false borax made of alum, saltpetre, soda or tartar. He refers to three methods for separating borax from surrogates: Shape of the crystals, behaviour when exposed to heat, and ability to flow and "liquefy" metals (Krünitz 1788). In addition, Paracelsus and Zedler mention different kinds of surrogate borax (Zedler 1732-1754).

It is remarkable that Heraclius as well as Theophilus uses a more careful definition. Heraclius writes *„accipias illum liquorum qui vocatur bures"* (*„and then take the liquor which is called borax"*), while Theophilus formulates *„accipe gummi, quod vocatur parahas" ("take the resin called borax"*).
Referring to Al Razi, relating willow gum to the borates, an explanation of the term *gummi* might be found in the reference. Did Theophilus refer to a plant gum or Gummi Arabicum as C. R. Dodwell suggests (Dodwell 1961), and called it transmogrified *barabas* in imitation of Arabic terms? Could Theophilus in the beginning of the 12th century be aware of Al Razi's works? Did he refer to a mixture of plant gum and some inorganic flux similar to the numerous surrogates mentioned in the references? Even today, borax is sometimes mixed with traganth (Maryon 1954).
Has such a technique been used in making the niello of the shrine of Vitus?

6. Conclusion

The study of technical manuscripts revealed facts about the knowledge and the use of borax in the medieval Arabic world and Europe until the beginning of the 19th century. Availability of borax north of the Alps in medieval times cannot be proved by literature, due to mistakes of transcription and translation, incorrect descriptions or confusion of terms.
Mention of the term borax in the manuscripts does not inevitably mean that borax was actually used. Therefore, the recipe of the shrine's niello might correspond with the recipe given by Theophilus, even if no content of boron was detected. It is not sure whether Theophilus was speaking of borax or not. As well there is a possibility that the niello contains boron, which could not be detected by analysis.

However, the situation in the matter of the analysed content of boron in the enamel is clear. Borax does not seem to be used for enamel work before the 17th century, but only for refining and soldering techniques as well as for nielloeing. As a conclusion, the sheets of the shrine's lid cannot considered to be authentic. According to our knowledge, they were not produced before the 17th century. This is suggested by the detected contents of boron in the glass, in combination with relatively reliable references.

This case study is not able to sketch the whole situation, but it might throw some light on the topic of borax in early European goldsmith's work. Numerous but unreliable references of that time do exist, and knowledge of the usage of flux in early times is still poor. It is desirable to carry out further analysis referring to the usage of flux. As demonstrated in this work, it may offer information not only concerning the production technique but also regarding dating or authenticity.

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Stabilization of a wrecked and corroded aluminium aircraft

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Abstract

In 1984 the Australian War Memorial (AWM), Royal Australian Air Force and Royal Australian Navy recovered a crashed Japanese Army Air Force Nakajima Ki 43 II "Oscar" fighter aircraft from Papua New Guinea. The aircraft had crashed at the end of an airfield and had been sitting in swampy ground since 1944, and had subsequently corroded and suffered extensive deterioration. In 1996 electrolytic treatment development for corroded composite metal artifacts had reached the stage where it was feasible to electrochemically treat "Oscar " without needing to breakdown the aircraft into small separate components. An above ground swimming pool was erected and filled with a solution of citric acid, sodium hydroxide and water. An electrolytic cell was formed by using expanded stainless steel mesh as anodes and making the aircraft the cathode. An applied potential of approximately 1.15 volts, (with respect to a mercury sulphate electrode) was administered for one month. Electrolysis was followed by a further polarization in fresh water for one week to remove the chemicals. Upon removal from the pool the aircraft was cosmetically treated to remove flash rust and finally coated with wax. During the treatment samples were taken from the pool to monitor pH and concentrations of dissolved chloride, iron, copper and aluminium.

Keywords:: Aluminium, citric acid, electrolysis, composite materials ,aircraft.

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1. Introduction

The AWM has in its collection a number of corroded aluminium alloy/metal composite objects that were recovered from aqueous saline environments. Such objects can continue to corrode quite readily after being removed from aqueous environments, even in relative humidities below 35% due to chloride contamination in crevices and the prevalence of bimetallic couples. (Evans, 1960)

A method for stabilizing corroded aluminium/copper alloy objects by using an amonnia-ammonium sulphate buffer in deionized water was developed by MacLeod in 1982. The method works by dissolving copper corrosion products and precipitated elemental copper. This method works well when there is only one alloy involved, but is not satisfactory when other alloys and metals, particularly copper, are part of the object.

In 1991 the AWM (in conjunction with Electricité de France and Research School of Chemistry, Australian National University) began developing an electrochemical method to treat corroded aluminium alloy/metal composite objects. The method was based on doctorate thesis work by Degrigny in 1990. Research has been supported by donations from The International Group for Historic Aircraft Recovery (TIGHAR) and the Historical Aircraft Restoration Society (HARS).

The method is still being developed and perfected, but has reached the stage where treatment of large composite aluminium/metal objects is feasible and can be confidently carried out with minimal risk to the object. (Adams, 1992 and 1993, Hallam et al 1997)

Over the past five years the size of objects treated has ranged from small pieces of aircraft and ship fittings through to largely complete aircraft engines. This paper describes the treatment of a wrecked and corroded Japanese WWII Nakajima Ki -43 II Hayabusa (Peregrine Falcon) fighter aircraft. This was the latest and largest aluminium alloy/metal composite object to be electrochemically treated with the new method at the AWM.

History of "OSCAR"

The Nakajima Ki-43 II Hayabusa (Peregrine Falcon) was the principle fighter aircraft used by the Japanese Army during World War 2. The Ki-43 was comparable in most respects to the better known Mitsubishi ‘Zero’ employed by the Japanese Navy (Angelucci and Matricardi, 1988).

During the war the Allies used a system of Christian names to make identification and reporting of Japanese aircraft simpler. Female names were allocated to bombers, flying-boats and land based reconnaissance aircraft. Female names beginning with ‘T’ were allocated to transport aircraft, and male names were allocated to fighters and seaplane reconnaissance types. Thus the Nakajima Ki-43 Hayabusa was known to the allies as “Oscar”. (Okumiya et al,1958)

Oscar serial No.5465 was probably built in 1943, and was based at the Sek Fighter Airstrip at Alexshafen, near Madang, New Guinea. The aircraft was damaged during a landing accident in 1944, and after being stripped of useable equipment it was abandoned at the end of an airfield in swampy ground. Over the next 40 years Oscar was subjected to
aerial attack, grass fires, vandalism, monsoon rains and mud. Subsequently corrosion and decay completed the state of the aircraft as found..

In 1984 the Australian War Memorial, Royal Australian Air Force and Royal Australian Navy recovered Oscar from Papua New Guinea. During recovery it was dismantled into three main components consisting of the wing and cockpit section, rear fuselage and empennage, and engine. Since then the aircraft has been kept in mostly inadequate storage, adding to the slower corrosion process.

2. Condition

To facilitate recovery and transport, Oscar was dismantled into three major pieces, comprising the wings and cockpit (approximately 10 metres x 3 metres x 1.4 metres), rear fuselage and empennage (approximately 4.4 metres x 3.7 metres x 1.6 metres) and the engine and propeller (approximately 2.3 metres diameter x 1.5 metres.

Most of the corrosion of the aluminium had occurred on the lower surfaces of the aircraft, caused by resting in mud. The upper surfaces of the wings and horizontal stabilizers were also corroded, probably from the accumulation of rotting fallen vegetation. The vertical surfaces of the cockpit and fuselage sides are remarkably corrosion free, however the site from where the aircraft was recovered was in a salt air and salt water environment, so saline corrosion was expected.

All the ferrous alloys, with the exception of the stainless steel fittings, had medium to heavy surface corrosion. The lead-alloy counter-weights located on the leading edges of the elevators had only light corrosion.

Very few rubber and plastic parts remain on the aircraft. Those parts that do remain appear to be stable. Nothing remains of the linen fabric that would have covered the control surfaces.

Some original paint still survives on the aircraft. This paintwork includes Unit markings on the tail and rear fuselage, yellow leading edges on the underside of the wings, stencilled serial numbers and jacking point indicators. Hinomaru (the national Japanese military markings - large red circles with white outline) on the fuselage and wing undersides are still visible. The typical blue-green coating used by the Japanese as a corrosion inhibitor for the internal surfaces was also found in various locations. No evidence was found of camouflage paint.

Pencilled hand written numerals and Japanese characters were found inside the cockpit and rear fuselage. It is believed that these numbers were used as an aid in the manufacturing and assembly process.

Surprisingly, the main undercarriage olio legs are still leaking oil and on examination the pistons were found to be only lightly corroded.

There was a lot of storage dirt, dried mud, vegetation, loose corrosion products and metal fittings, throughout the aircraft. Two large snail shells and two spent 0.5" bullets (a common machine gun calibre used by the USA and allies) were found amongst the debris.

Much of the airframe is buckled and twisted, and there are many holes in the skin. Some of this damage is a result of the landing accident and subsequent Japanese salvage, and Allied air attacks. Other damage is a result of vandalism before the plane was recovered, and damage incurred during the recovery operation. Considerable damage was caused by Australian Customs when the wreck entered Australia. A number of holes were punched through the top skin of the wings by Customs to ensure adequate fumigation. One wonders why this was necessary. If fumigation gases couldn’t penetrate a sealed space, then there seems to be little chance of an organism doing so.

3. Treatment method

At the time of writing, only the wing and rear fuselage sections have been treated. Normally the process used involves a series of steps, which are:

1. mechanical cleaning to remove debris and loose corrosion and accretions

2. masking of paint and other features that need to be protected from chemicals

3. polarization in a solution of metasilicate, polyphosphate and bicarbonate to produce a stable magnetite coating on ferrous components

4. washing with fresh water and further mechanical cleaning to remove accretions loosened in step 3

5. polarization in a solution of citric acid and sodium hydroxide to remove chlorides and aluminium corrosion

6. polarization in fresh water to remove above chemicals, and

7. drying, treating of flash rusting and application of a protective coating to reduce the incident of future corrosion.

For the treatment of Oscar's wing and rear fuselage, it was decided that step 3 would be deleted from the process. There were several reasons for this decision. To include step 3 would have required an additional 110, 000 litres of water plus the associated chemicals to make up the two extra baths, and the additional time. All this would have involved considerable expense. Also, the disposal of large volumes of high pH solution would pose problems. The fact that the amount of ferrous alloys in the two sections is relatively small in relation to the amount of aluminium alloys made it hard to justify the addition expense, time and disposal problems presented by step 3. When the engine and propeller section is treated, step 3 will be included, as the solution volumes will be more manageable, and the ferrous/aluminium alloy ratio is higher.

The difficulty in the treatment of Oscar was not so much the process itself, but the logistics involved. Lifting a fragile object that is 10 metres long, 3 metres wide and weighing almost a tonne requires considerable forethought and planning. The sections needed to be lifted 1.8 metres in order to get them into the pool, and during lifting they had to be kept level and balanced. Much time and testing was involved in identifying suitably strong lifting points and arranging lifting tackle to achieve a safe, level lift.

3.1 Preparing for the treatment

3.2 Treatment container

In order to give Oscar an electrochemical treatment, a suitably large treatment tank was necessary. Factors which influenced the final choice of treatment tank were size, initial cost, capital works needed, resistance to the chemicals to be used, ease of assembly and disassembly, accessibility to the solution during treatment, and ease of disposal by resale at the end of the project. Several options were investigated including purpose built tanks, below ground fibreglass swimming pools, and above ground swimming pool kits.

A purpose built tank proved to be too costly, required capital works to the floor of the treatment area, was too high to allow easy monitoring and sampling, and would not be easy to dispose of at the end of the project

Fibreglass in-ground swimming pools were cheaper than the above ground tanks, but would require considerable earth works. If used above ground, problems with stability and strength of the pool were likely as well as height problems mentioned previously. Resale value of an in-ground pool was better than a purpose built tank.

Above ground swimming pool kits offered the best compromise. They are considerably cheaper than the above two options, do not require any capital works, are relatively simple to transport, position, erect and dismantle, and are popular and cheap enough to make disposal relatively easy. Above ground pools are available with a maximum depth of 1.2 metres. This meant that it would not be possible to completely immerse Oscar during treatment. This was accepted as a compromise, as most of the area that would be exposed was only lightly corroded. A partial solution to this problem will be dealt with in a later paragraph..

Samples of pool lining material were obtained and were tested for compatibility with the chemicals to be used. The samples showed no change in appearance, flexibility or strength after six months soaking in the solutions. Upon completion of the tests a 12 metre x 4.5 metre x 1.2 metre above ground pool kit was purchased.

The pool was positioned in the Treloar Centre Conservation Annex, directly under an overhead gantry. Normally when erecting above ground pools, the framework is buried in ditches. Obviously, this was not possible on the concrete floor of the building, so 2,500 house bricks were donated by Nubrik Pioneer Building Products to build the floor up to the level of the framework. The bricks and frame were covered with sand.

3.3 Anodes

Expanded Stainless Steel mesh was used for the anodes. The mesh was cut to the approximate size and shape of the Oscar pieces and attached to wooden frames to give approximately 30 cm clearance from the Oscar pieces. The anodes/frames used under Oscar were positioned in the pool before it was filled, all electrically connected, and weighted down with bricks.

The anodes for the upper and vertical surfaces, and inside the fuselage and cockpit were tied to the Oscar pieces and electrically connected before each piece was lifted into the pool.

In order to electrically connect all of the anodes, stainless steel tabs were soldered to insulated copper wire. The soldered region was encased with epoxy resin to avoid failure caused by chemical action. The tabs were attached to the mesh using stainless steel screws.

3.4 Preparation of solution

In order to obtain the desired pH and molarity, it was necessary to measure that amount of water put into the pool, so that the appropriate amount of citric acid and sodium hydroxide could be calculated. A water meter of the types that are connected to suburban houses was attached to the hose used to fill the pool. The desired pH was 5.4, and the citric acid concentration was 0.055 moles per litre.

Mixing approximately 800 Kg of chemicals with 55,000 litres of water in a swimming pool poses problems that one doesn't normally encounter in bench-top conservation. It was not possible to add the chemicals directly into the pool, because there was a risk that localised concentrated sodium hydroxide would burn through the pool lining. Another problem is that both the sodium hydroxide and the citric acid tend to form large lumps which dissolve very slowly. To solve this problem, water was circulated from the pool through two large water tanks where the chemicals were gradually added over a period over several days.

3.5 Preparations of “Oscar”

Before immersion the aircraft was thoroughly examined to remove loose pieces of metal and other foreign material. It was during this stage that the two spent 0.5" bullets were found in the floor of the cockpit. The bullets were probably from Allied fighter aircraft that strafed the airfield.

After all loose material was removed the aircraft was washed with a K'Archer pressure spray to remove as much dirt and loose corrosion as possible. The pressure used was limited to approximately 60 psi, so that fragile metal parts and paints were not damaged.

Before immersing the aircraft into the solution, the original paint and pencil markings had to be protected. Previous experience has shown that if the paint is not protected it will swell and loose adhesion with the aluminium substrate. A coating of microcrystalline wax, followed by a sprayed layer of clear acrylic lacquer was applied over the areas to be protected.

Small alligator clips were soldered onto copper wire to electrically connect all parts of Oscar. Series of 10 clips were soldered to two metres lengths of wire to make handling and installation easier. Each end of the wire was fitted with an in-line plug to simplify joining of the wires to each other. The soldered joins were encased with epoxy resin as mentioned previously. Ten large battery clips, each with a separate wire were also made to attach to large ferrous fittings of the aircraft. Approximately 200 metres of insulated copper wire, 700 small alligator clips and 10 large battery clips were used in total.

As mentioned, the swimming pool was not deep enough to completely immerse the Oscar pieces. This presented a potential problem of tide marks resulting from etching and/or corrosion at the solution/air/metal interface. To prevent this, the exposed parts were covered with Engineers Felt and the solution pumped over the felt. The aim was to keep the exposed parts saturated with the solution. A garden hose with small holes every 10 cm or so was placed under the felt on the rear fuselage section, which was treated first. This solution did prevent etching and corrosion at the interface zone, but resulted in some distinct staining associated with the hose holes. For the cockpit/wing piece, a garden soaker hose was used on top of the felt. This worked much better, with the staining being much less distinct. In both cases, visible etching and corrosion was avoided, although there is a visible stain at the interface zones. This is probably due to lack of electrochemical action above the solution level.

3.6 Treatment

The treatment was instigated by a curatorial request to provide a stable displayable aircraft in relic condition. Oscar was still showing active corrosion and corrosion products and all the species needed to be treated to achieve management requirements.

Once the solution had been mixed and anodes positioned, the rear fuselage section of Oscar was immersed in the pool. All of the anodes were connected to the positive terminal, and Oscar connected to the negative terminal of a Hewlett Packard 6642A System DC Power Supply. An Activon AEP114 Single Junction Hg/Hg_2SO_4 reference electrode connected to a Hewlett Packard 34401A Multimeter was also connected to the negative terminal to measure the potential of the system. A potential of approximately 1.10 - 1.20 volts (with respect to a Hg/Hg_2SO_4 electrode) was applied to the system, as influenced by the treatment to another aircraft part by De Grigny while studying at the AWM. The potential was monitored and adjusted closely for the first two hours until the system had stabilized, and then checked and adjusted on a daily basis. A pump was connected to the hose on the exposed tail to ensure that it was kept wet. Two other pumps were used to keep the solution circulating, thus avoiding localised increases in pH. The temperature of the solution was initially 17^{o}C and rose to 19^{o}C after one month. Figure 1 shows the rear fuselage section during treatment.

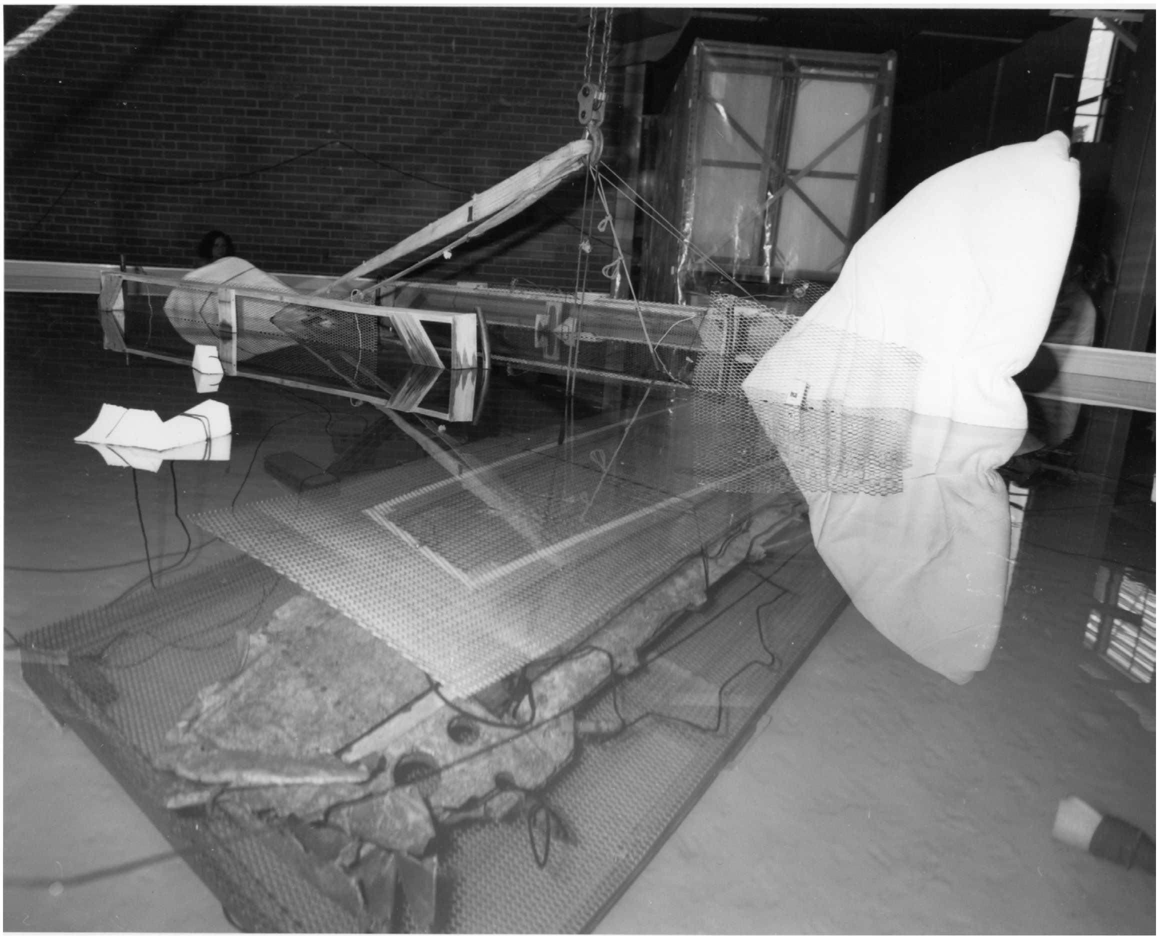

Figure 1. Oscar rear fuselage and empennage during treatment

At weekly intervals the rear fuselage was lifted out of the pool and inspected for progress of the treatment and unexpected corrosion development. After one month all ferrous corrosion and white and blue/green aluminium corrosion products had disappeared, and a thin layer of non-adherent black smut, assumed to be copper oxides, had settled on the rear fuselage. Biological activity had also appeared in the solution. No significant increase in either pH or chloride levels in solution were recorded, so the rear fuselage was removed and the black smut washed off.

The pool was drained, cleaned and refilled with clean water, and the rear fuselage re-immersed for one week to remove remaining traces of the first solution. The same potential as above was applied to the system. Upon removal from the pool again, the rear fuselage was encased in polyethylene and dehumidified for two weeks to completely dry it. During this period, flash rusting occurred on all ferrous parts. These were treated with 5% w/v Tannic acid in ethanol. The rear fuselage was then sprayed with Dinol AV5B inhibited wax to protect it from future corrosion.

The treatment of the wing/cockpit section of Oscar proceeded in same way as the rear fuselage. Biological growth was more prevalent during this treatment, probably because the temperature of the solution had increased to 22^{o}C. The treatment time, pH, and chloride levels were the same as used previously. Figure 2 shows the wing/cockpit section being placed in the empty pool to check the position of the bottom anodes.

Figure 2. Oscar wing and cockpit section in the pool to check the position of the bottom anodes.

During the rinsing stage, it was noticed that small white spots were starting to appear on the wings. This indicated that pitting corrosion was occurring, suggesting that the potential of the system was not correct.. All electrical connections were checked and found to be in order. The reference electrode was then checked and found to be giving inaccurate readings. This is thought to be due to contamination from biological growth blocking the ceramic frit. The correct potential was reapplied, and the section was left for another week. After removal, the wings were scrubbed to remove the remaining white corrosion products, and then dried, tannated and waxed in the same way as the tail section above. Figure 3 shows the wing/cockpit section after treatment.

Figure 3. Oscar cockpit section after treatment.

4. Discussion

4.1 Analyses

Before treatment, samples of the main aluminium alloys were taken and analysed to determine alloy types. The samples were analysed by EDXA in a Scanning Electron Microscope. The results indicated that the majority of the alloy is approximately equivalent to a 2000 Series aluminium alloy, and the main spar composition is approximately equivalent to a 7000 Series alloy.

Samples of the pool solution were taken daily to measure pH and chloride levels. Over the course of the treatments neither the pH nor chloride levels rose significantly. Normally in this type of treatment both levels would be expected to rise. With this particular treatment the lack of change in pH can be attributed to the sheer volume of solution compared to the surface area of the object. Likewise, the volume of solution compared to the amount of chloride present in the objects meant that the change in chloride levels in the solution was difficult to detect.

Further analysis of the solutions samples to measure concentrations of dissolved aluminium, copper and iron has yet to be undertaken. Atomic Absorption Spectroscopy
will be used for these analyses. Ideally, these analyses should be conducted as soon as the samples are taken, so that the chemical activity can be monitored and the solution

changed as soon as the solution has become depleted. Again, however, the sheer volume of the solution meant that chemical depletion was not anticipated as a problem.

4.2 Problems Encountered During the Treatment.

A problem that has plagued the treatment throughout its development has been the corrosion and subsequent failure of the alligator clips. Both chrome plated and zinc plated clips are prone to failure. The use of stainless steel clips was considered, but was not adopted due to the high cost and poor availability. Protective solid coatings for the clips was also considered, but problems with conductivity between the clip and the object, and cracking of the coatings on the springs precluded this option.

A coating was needed that would conduct electricity, be flexible enough to cope with flexing of the springs, be cheap and easy to apply, and provide protection from corrosion.

The alligator clips were dipped in molten Vaseline Petroleum Jelly. This made the clips a little difficult to apply. The performance of the clips coated with vaseline was not perfect, but the number of clips that failed was substantially reduced.

Because the pH of the solution is fairly neutral, and citric acid is biodegradable, algal and fungal growth occurred in the solution. The temperature of the solution, which was about 22°C also exacerbated the problem. Biological growth in the solution is undesirable because it consumes the citric acid, produces by-products whose effects are unknown, lowers the clarity of the solution, and produces offensive odours. In this treatment it also contaminated the reference electrode. Biological growth could have been avoided by adding a biocide to the solution, but this would then pose problems with the disposal of the used solution. Without the biocide, the used solution could be disposed of in the sewerage system, where it would go through the water treatment plant to be processed.

Visibility of the object through the solution dropped quite dramatically due to a combination of biological growth and the dissolution of mud that was still trapped in the wings.

During the treatment of the wings/cockpit section, some electrical problems were encountered. Disruptions to the electrical supply due to building works meant that for several periods up to two hours the object was not protected electrically.

Contamination of the reference probe by biological material in the pool also caused an incorrect potential to be applied to the wing/cockpit section during the final rinsing stage. This resulted in some minor pitting of the aluminium.

5. Conclusions

Despite the problems encountered above, the overall treatment of Oscar was considered a success. The total treatment time for Oscar, less the motor which is still to be treated, was seven months, including the erection and dismantling of the pool. The development of the treatment method has still to be perfected, with further work being needed to reduce the failure rate of the alligator clips, to eliminate flash rusting of ferrous parts, and finding environmentally friendly ways to control biological growth in the solution. The stabilization of Oscar shows that large metal composite objects can be relatively quickly and successfully electrochemically treated using biodegradable solutions, provided that of the pH, molarity and potential of the system is carefully controlled.

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On again, Off again - Cathodic protection of a lead and ceramic water closet during desalination.

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Abstract

The inter-colonial passenger ship, *SS City of Launceston*, sank in Port Phillip Bay, Victoria, Australia in 1865. Two earthenware and lead "Hopper" style water closets (toilets) were raised from the wreck in 1996 and one in 1999.

One toilet had a large copper flush pump attached to the lead. The toilet was immersed in tap water for desalination of the ceramic but after a short time active corrosion was visible on the lead. Corrosion of the lead continued even after the flush pump became detached from the toilet. The possible reasons for this corrosion are discussed.

Impressed current cathodic protection was applied to the toilet using anodes of platinum coated titanium. Australian Standards for cathodic protection were followed but corrosion continued. The final system applied an impressed current to shift the on-potential 150mV in the negative direction from the depolarised potential, with current as low as possible. This, combined with a water mixer to increase diffusion, halted the majority of the corrosion. The desalination of the ceramic and conservation of the toilet was completed successfully after 6.5 years of treatment.

Key words: lead corrosion, ceramic desalination, cathodic protection, maritime conservation

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1. Introduction

An inter-colonial passenger steamer, *SS City of Launceston* was partially excavated by the Maritime Heritage Unit, Heritage Victoria between 1996 and 2000. The ship was the flagship and the latest addition to the small fleet owned by the Launceston and Melbourne Steam Navigation Company (LMSNCo). It was built and fitted out by Blackwood and Gordon, Newark, Glasgow in 1863 to the order of the LMSNCo in Tasmania, Australia for passenger and freight transport between Melbourne in Victoria and Launceston in Tasmania. For the time it was a modern, luxuriously appointed ship.

> "…fitted up with all the modern improvements for comfort of passengers of all classes … (with)…fittings (that) are of a most substantial character and at the same time are ornamental." (Launceston Examiner, 1863).

The *SS City of Launceston* sank in Port Phillip Bay, Victoria in 1865 after a collision with the SS Penola.

Among the best surviving examples of the "ornamental appointments" are the ship's "heads" or toilets. Two ceramic earthenware and lead "Hopper water closets" (Historic

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Houses Trust, 1984) were raised from the wreck in 1996, and one in 1999. The bowls are made of glazed earthenware with an elaborate underglaze blue-and-white transfer print pattern. The bowl surrounds, down pipes, flush plates and pipe from flush pump to toilet are made from lead. Two of the toilets had a large copper flush pump attached to the lead. The pumps are made from a hollow copper cylinder containing a lead, iron, leather and wood mechanism. The base flange of each toilet was attached to the wooden decking with copper alloy tacks.

Two of the toilets (124.00009 and 124.00318) were in poor condition with considerable loss of ceramic and distortion of the lead (see Figure 2). However one toilet (124.00010) was in better condition (see Figure 1) with an intact, elaborately patterned ceramic bowl. This object generated considerable public interest and publicity both at the time of its excavation, and up to the present day (unknown, 1997; Brown, 2003), with the pattern and appearance of the ceramic being the focus of most attention. It was clear that the conservation of the ceramic was critical. The preservation of the ceramic and lead components of the most intact toilet (124.00010) is the focus of this publication.

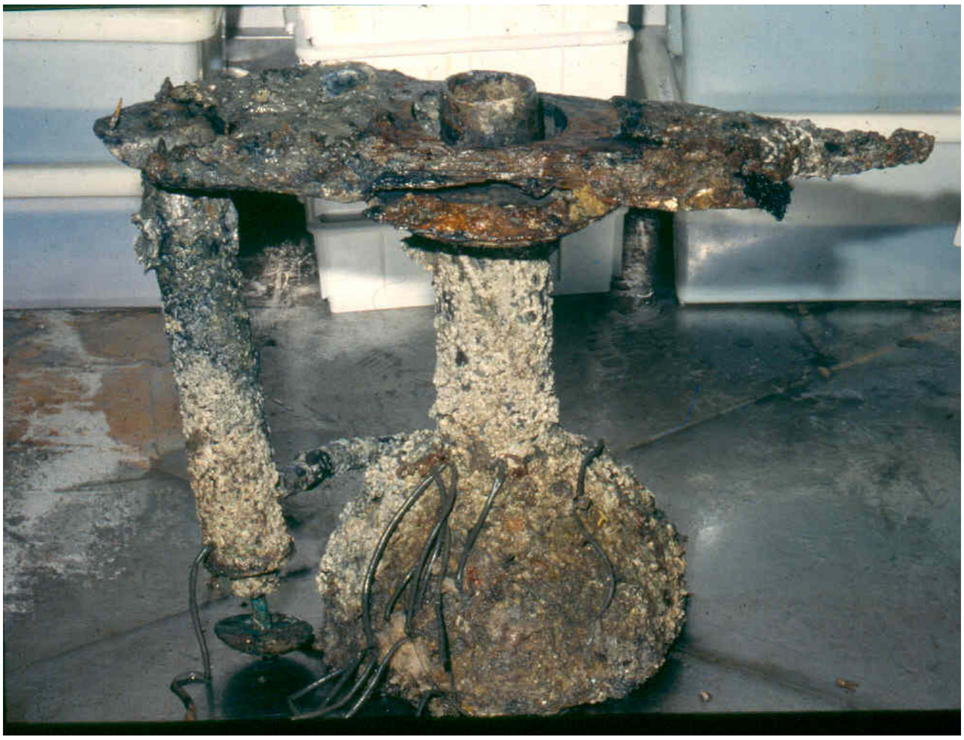


Figure 1 – Toilet 124.00010 After excavation

Figure 2 - Toilet 124.00318 After excavation

2. Initial treatment and decisions

When lifted from the sea all three toilets were covered with heavy marine concretions, sea life and silt. In aerated seawater lead is protected by the formation of insoluble lead sulphate, $PbSO_4$, (North and MacLeod, 1987). On site and during transportation to Heritage Victoria's conservation lab in Melbourne, the toilets were kept wet with seawater. Once back at the laboratory the bulk of the heavy marine concretions, sea life and silt were removed manually using a variety of plastic and metal tools and washing. The toilets were initially placed in a polypropylene tank containing a mixture of 1:1 seawater: tap water. After one week this was replaced with 100% tap water to start the standard ceramic desalination process (Pearson, 1987) while treatment decisions were formulated. Tap water was chosen because purified water is known to corrode lead (North 1987). The pump became detached from toilet 124.00010 in 1997 during x-raying and subsequent handling, and was stored and treated separately.

Initially it was intended to disassemble the toilets to separate the ceramic and lead since both required very different stabilisation treatments. Lead recovered from seawater is relatively stable, but because the seawater can penetrate porous ceramics, these require desalination to remove soluble salts (North, 1987; Pearson, 1987). Heritage Victoria' s laboratory policy is to desalinate ceramics recovered from marine sites until three consecutive monthly chloride readings are at 10ppm or lower.

It was possible to remove the ceramic fragments from toilets 124.00009 and 124.00318 however it was not possible to do this for the intact toilet 124.00010. The lead flush plate was bolted through the ceramic to the lead with copper alloy nuts and bolts, two per plate. Attempting to undo these bolts, while theoretically possible was considered to pose an unacceptable risk to the ceramic and soft lead. Unlike the toilets from the *CSS Alabama* (Mardikian, 1997), the lead was in good condition and firmly attached to the whole of the ceramic, possibly applied with heat. These toilets did not have cast iron bases whereas those from the *CSS Alabama* did.

The decision to desalinate the ceramic leaving it attached to the lead complicated the treatment considerably. At the same time (about 12 months after excavation) significant amounts of active lead corrosion became visible on the lead and in the tank containing the toilet. After discussion (MacLeod, 1997) an attempt was made to halt the corrosion by creating 500ppm solution of sulphate ion (SO_4^{2-}) in tap water using sulphuric acid. However corrosion continued and we were concerned about the possibility of introducing sulphate salts to the ceramic, which could deliquesce and crystallise in the future (Halsberghe, 2002). Other inhibitors such as carbonate had similar potential salt problems to the sulphate. We considered that introducing more soluble salts would be counter-productive to the overall aim of desalinating the ceramic. Therefore the toilet was placed in tap water without inhibitors.

The use of a sacrificial magnesium anode was also considered however magnesium anodes are known to be rapidly consumed in cathodic protection situations (Standards Australia, 1992) and this could have introduced unacceptable levels of magnesium ions or magnesium salts to the ceramic. Instead, after advice from a corrosion engineer (Robilliard, 1996), the staff at Heritage Victoria collaborated with a corrosion engineering company, Remedial Engineering, to develop an impressed current cathodic protection system.

3.1 Corrosion

The reasons for the occurrence of the active corrosion on toilet 124.00010 are complex and have not been fully resolved. As the toilet without a pump (124.00009) that was excavated did not show this corrosion, it was assumed that the presence of the copper pump on toilet 124.00010 had led to the establishment of a galvanic cell i.e. anodic sites on the surface of the lead. There is a large difference (0.468V) between the standard Electromotive Force Potentials (emf) for copper (+0.342V) and lead (-0.126V) (Jones, 1996) indicating that copper is cathodic to lead, and therefore one would expect the corrosion of the lead to be accelerated when attached to copper. Even when the pump was removed the lead continued to corrode. However, when the third toilet (124.00318) was excavated in 1999 and placed into tap water, no visible corrosion occurred despite the presence of the copper flush pump. The copper alloy bolts remained on all three toilets during treatment. Given that they were present on all three toilets it appears that their presence did not contribute greatly to the corrosion of toilet 124.00010.

Other possible reasons for the differences between the corrosion rates of the three toilets could be:

3.1.1. Degree of de-concretion

Initially toilet 124.00010, being the most photogenic, was more thoroughly de-concreted than the other two toilets. All the organic marine life was removed from the toilets to limit damage from organic acids (North 1987), while small amounts of carbonate concretions (coral and shell) remained. However, toilet 124.00318 was de-concreted to a similar extent three years after excavation and is not showing any visible corrosion nearly one year later. Therefore, it is unlikely that the degree of de-concretion affected the corrosion. It is possible that the presence of carbonate concretions could have promoted inhibition of the lead corrosion, as it is known that chalk can actively promote passivation of lead roofs (Bordass, 1998).

3.1.2. Composition differences between the toilets

Preliminary analysis of the metal composition was done by Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). Initial readings indicated both toilets (124.00009 and 124.00010) were about 99.8% lead with minor additions of copper, tin and other metals. Ideally further analysis would be done running repeat samples and including the third toilet (124.00318) in the testing.

3.1.3. Compositional differences within the lead of toilet 124.00010

There are several bands of light and dark coloured metal visible on the body (see Figure 4). It is possible that lead of different compositions may have been used to make the lead component. This may represent different pours during the casting process, perhaps due to crucible size or other factors. Toilet 124.0009 only shows one different coloured band and none are visible on toilet 124.00318. We hope to be able to analyse the various metal compositions in the future.

3.1.4. Effects of chlorides

The chlorides diffusing out of the ceramic increases the chloride content in the desalination water. The increase in chloride level may have an influence on the corrosion rate by increasing the conductivity of the water and breaking down the protective films initially produced by other seawater constituents (Burns, 1948). The other two toilets had far less ceramic remaining and this would have led to less chloride being present in the tap water in the tank.

4. Potential measurements

To try to understand the electrochemical state of the toilet, a single set of corrosion potential (Ecorr) measurements were taken using a Saturated Calomel Electrode (SCE) as the reference electrode. Using a Digital Multimeter set on D.C voltage, the negative (COM) terminal was connected to the toilet with an alligator clip above the water line, and the SCE was connected to the positive (V) terminal. This set up makes the toilet negative to the SCE. [When using digital multimeters it is also possible to take the readings by connecting the negative terminal to the electrode and the positive terminal to the structure because digital meters will display negative readings. However when using an analogue multimeter our set up is essential as analogue multimeters do not have a negative scale, and therefore users would not get a reading if the more conventional connection format was followed.] The SCE was then positioned over various parts of the toilet and the potentials recorded at each location. These readings were taken for both toilets 124.00009 and 124.00010 and the results are summarised in Table 1 below. The SCE is +241mV with respect to (wrt) the Standard Hydrogen Electrode (SHE). Standard electromotive and Pourbaix data are given wrt the SHE in theoretical literature (Pourbaix, 1974) but the SCE is often used in real applications because of its sturdy nature. Values in cathodic protection literature are generally quoted wrt the Saturated Copper/Copper Sulphate (Cu/CuSO4) electrode, which is 74mV wrt SCE (Jones, 1996). Where possible all values in this paper have been converted to SCE.

The toilets were immersed in Melbourne tap water for the desalination process. Analysis of Melbourne water based on the average of July 1999 to June 2004 data (Melbourne Water, 2004) gives the following parameters:

Total dissolved solids (TDS) mg/L	35 to 90
pH range:	6.9 to 7.8
Hardness range mg/L	12.0 to 25.0
Total alkalinity (as CaCO3) mg/L	11.3 to 14.0
Specific Conductance µS/cm	55 to 138
Sulphates mg/L	0.8 to 8.3

In applying these parameters using the median value of the range and assuming a temperature of 25°C in the room, a calculated Langelier Saturation Index (LSI) returns a value of -2.60.

The LSI is the difference between the pH of a water sample, and the pH at which that water sample would be saturated in calcium carbonate (RMCC, 1999). A negative LSI means that the water dissolves calcium carbonate, and therefore passivation due to $PbCO_3$ film formation may be reduced. While the levels of sulphate in Melbourne water are very low, $PbSO_4$ could have been be formed on the lead by residual sulphates from the earlier inhibition attempt. However since corrosion continued it seemed likely that this layer was now either absent or damaged.

The resistivity of the water gives an indication to the rate of corrosion that may occur. The resistivity of Melbourne tap water calculated from the Specific Conductance parameter (Melbourne Water, 2004) ranges from 7,246 to 18,181 Ωcm. The corrosivity of the water based on the resistivity therefore ranges from moderate to slight (British Standards Institute, 1973).

The initial corrosion potentials were measured over various parts of the toilets (see Table 1). The range of corrosion potentials was -320 to -340mV wrt SCE across the stable toilet 124.00009. For the corroding toilet, 124.00010, readings with the SCE ranged from -285mV to -225mV over the exterior surface of the metal. Two equilibrium potential-pH diagrams were consulted (Turgoose, 1985), see Figures 3 and 4. However, since the composition of the desalination solution was not the same as either of these diagrams they could only be used as an indication of the corrosive behaviour of the two toilets. Since the potential range across the non-corroding toilet is much less (20mV) compared to the corroding toilet (60mV), it is possible that the higher emf is causing the corrosion and shifting the potential of the toilet into a corrosive zone. It is unclear what created this higher emf.

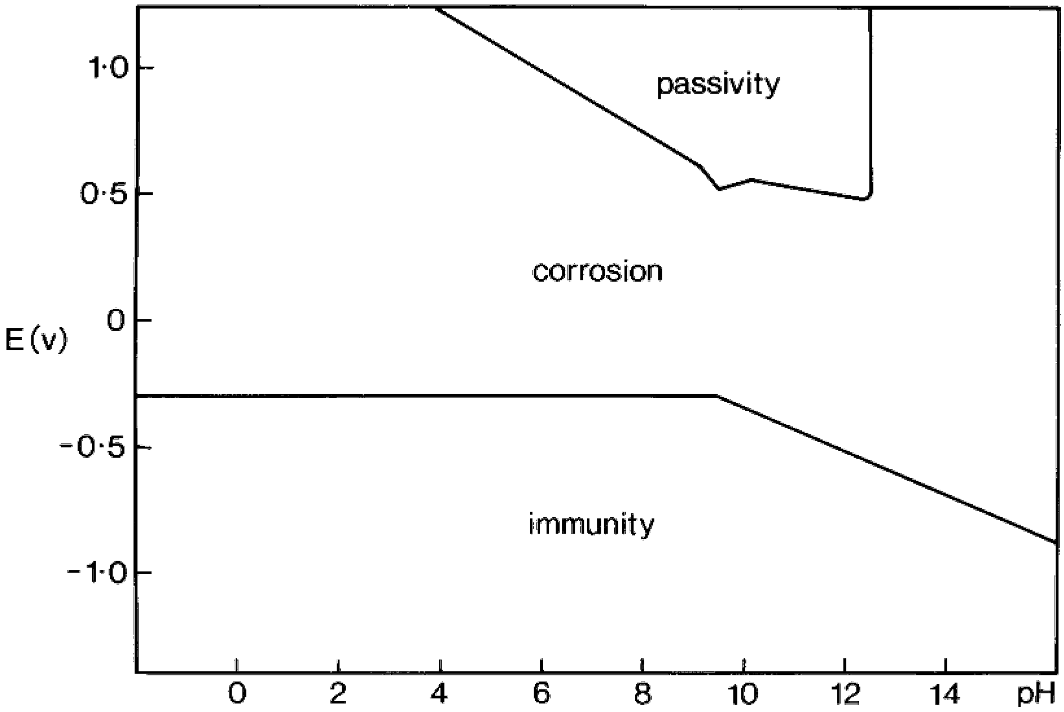


Figure 3 – Pourbaix diagram for the Pb-H2O system. (Turgoose, 1985). Used with permission of the United Kingdom Institute for Conservation.

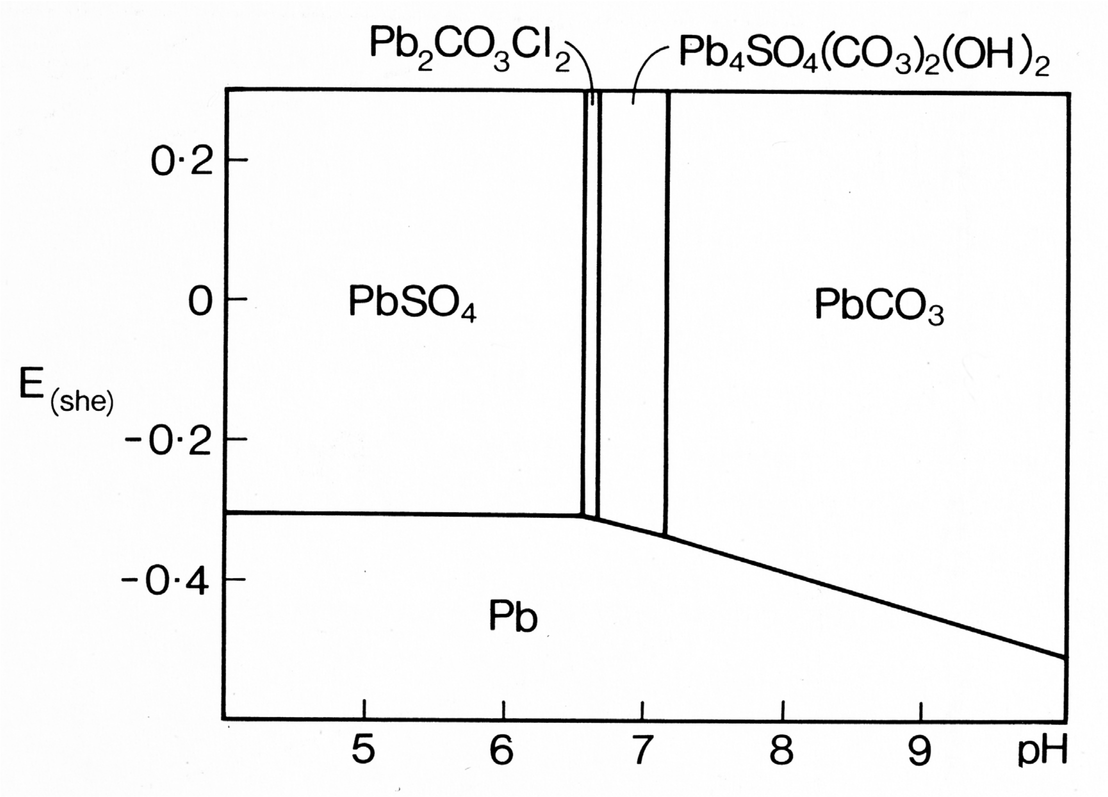


Figure 4 - Equilibrium potential-pH diagram for the Pb-H2O-CO2-SO4-Cl- system. Concentrations of species are similar to seawater. (Turgoose, 1985). Used with permission of the United Kingdom Institute for Conservation.

Table 1: Initial measured potentials across toilets 124.00009 and 124.00010

Reference electrode	Toilet 124.00010			Toilet 124.00009		
	Minimum measured potential (mV)	Maximum measured potential (mV)	Driving emf (mV)	Minimum measured potential (mV)	Maximum measured potential (mV)	Driving emf (mV)
SCE	-285	-225	60	-340	-320	20
Cu/CuSO4	-362	-302	60	-417	-397	20

4.1 Impressed current cathodic protection

The aim of cathodic protection is to provide excess electrons to the surface of the metal to be protected. This limits the oxidation of the metal (anodic reaction), instead favouring reduction (cathodic reaction). All corrosion reactions in water involve anodic and cathodic reactions such as (1) and (2). The application of a negative potential with excess electrons decreases the corrosion rate (Jones 1996).

anodic reaction $Pb_{(s)} \rightarrow Pb^{2+} + 2e^-$ (1)
cathodic reaction $O_2 + 2H_20 + 4e^- \rightarrow 4OH^-$ (2)

Two criteria for cathodic protection of lead are outlined in Australian Standard AS2832.1-2004

Clause 2.2.2.4. “The criteria for the protection of a buried lead structure is to maintain a potential on all parts of the structure equal to, or more negative than, -650 mV with respect to a copper/copper sulphate reference electrode when the structure is in aerated conditions…”

[-650 mV wrt Cu/$CuSO_4$ = -574 mV wrt SCE – this figure will be used henceforth.]

Clause 2.2.3. “The criterion for the protection of a buried structure shall be to maintain an instantaneous off-potential on all parts of the structure, which is at least 100 mV more negative than the depolarized potential”

However, these recommendations are for buried rather than immersed lead structures. Morgan (1987) also recommends a 100 mV negative polarisation of the potential of lead immediately after switching off the current for a buried structure. Similarly a British Standard (CP 1021:1973) identifies the cathodic protection current for lead as -0.6V wrt Cu/$CuSO_4$ without specifying if the lead is buried or immersed.
The Australian Standard AS2832.3-1992 for immersed structures does not give criteria for lead specifically but states:
“The accepted practice for the protection of mixed metallic structures is to maintain a negative potential at least equal to that required for the most anodic metal between all structure surfaces and a copper/copper sulphate reference electrode.”

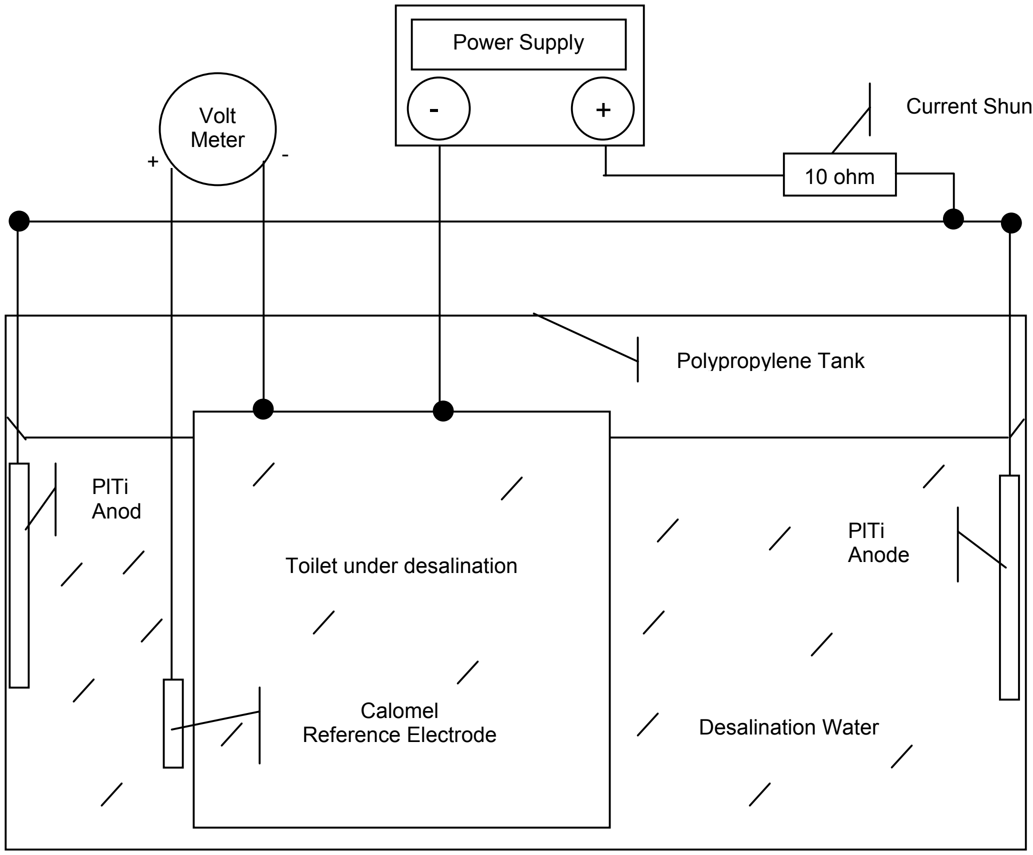
Pourbaix (1974) notes that lead can be cathodically protected by lowering its potential with respect to SHE to below -0.3V in acid or neutral solutions or below -0.4V to -0.8V (depending on the pH) in alkaline solutions. Despite some ambiguity across the various standards, the cathodic protection was set up following the criteria in clause 2.2.2.4 of AS2832.1-2004.

Figure 5 - Toilet 124.00010 in treatment tank, anodes visible

4.2 Cathodic protection method I

This method follows AS2832.1-2004 Clause 2.2.2.4. The toilet was placed into a 660 litre polypropylene tank that was filled with tap water. Eleven platinum coated titanium anodes were placed around the tank (see Figure 5). Platinised titanium anodes were used because they have a low Faraday loss, that is, a low loss of metal with current over time compared to zinc or magnesium (Standards Australia, 1992). This meant that the anodes would not contribute metal ions to the solution with the potential to enter the ceramic. The large number of anodes also kept the electron discharge low, thereby minimising metal ion release into solution; and gave a lower circuit loop resistance so that a lower voltage power source could be used. The anodes were connected via a 10□ resistor to limit current and enable a voltmeter to be placed across the resistor to accurately measure current. The resistance of the circuit was measured before connecting the power supply to prove circuit continuity. The loop resistance was 75□. The power supply was an EE1269 Cathodic Protection Power Supply. The "back emf" (voltage difference between the anode and the cathode) in this system was measured to prove a short circuit did not exist between the anode and cathode and was found to be satisfactory at 625mV. The power supply was operated in voltage control. The circuit was wired to the power supply as shown in Figure 6. The connection to the toilet was made using an alligator clip attached to the broken end of the flush pump. This was clear of the water and kept dry.

Fig 6 - Circuit diagram for the impressed current cathodic protection setup



The cathodic protection system was switched on and the output voltage increased in order to obtain an on-potential on the lead of -576mV wrt SCE, as specified in the Australian Standard. However, it was initially set at an on-potential of -530mV (rather than at -576mV) as it was considered the less negative level was more prudent as an initial attempt, and it could be gradually increased later if required. The applied protection current at this point was 21.5mA

Readings were taken daily (see Table 2) and show lead potentials remaining relatively steady but with the protection current gradually increasing. Following Ohms Law, this increase in current indicates that if the voltage was constant, the resistance of the system must have decreased. The decrease in the circuit resistance would occur with a decrease in the water resistivity (or increase in conductivity) probably caused by the increasing level of chlorides and other salts in the water.

Table 2 : Initial potential readings for toilet 124.00010

Date	Potential (mV)	Protection Current (mA)
18/2/98	-530	21.5
19/2/98	-540	21.3
20/2/98	-541	21.7
23/2/98	-539	22.9
26/2/98	-530	26.6
27/2/98	-534	27.3
3/3/98	-530	31.8

For eight days the water appeared crystal clear with small bubbles (presumably oxygen) coming off the anodes. But after 14 days the anodes were found corroding and crumbling on the base of the tank. There was thick, furry, silver-coloured lead corrosion over the side of the toilet and around the base. The system was turned off and small samples of corrosion products were removed and analysed using X-ray diffraction (XRD). The XRD results seem to indicate the active corrosion products on toilet 124.00010 were $Pb_3(CO_3)_2(OH)_2$ and $PbCl_2$. Other stable corrosion products found were common lead corrosion products, as found in aerobic, marine sites ($PbClOH$ and $PbSO_4$) and land sites ($PbCO_3$ and PbO_2) (North and MacLeod, 1987).

The pH and chloride ion concentration of the solution was measured (see Table 3). pH was measured using a TPS-Ionode pH meter and chloride readings were taken using a TPS-Ionode electronic chloride meter with a $Ag/AgCl_2$ electrode. It is possible the electrolytic decomposition of the water caused pH changes at the anode and cathode, but the measured pH of samples taken from near the lead and near the anodes at the side of the tank did not show a large variation.

Table 3: pH and [Cl-] of water samples taken from the tank holding toilet 124.00010 following cathodic protection

Sample	pH	[Cl-]/ppm
Near lead	5.2 - 5.3	46 - 47
Edge of tank	5.5	15 - 20
Tap water	6.5 - 7	22

Although the anodes had crumbled there was no evidence of titanium or platinum corrosion products from the XRD analysis. This may be because the corrosion products were soluble in water. The anodes were specified for 0.3mA/cm. Through a 10Ω resistor the maximum current reached was 31.8mA. Over 11 anodes this is 2.89mA per anode. As each anode is 200mm, equating to 0.14mA/cm, it appears that the anodes were not overloaded. However it is possible that the increasing current (caused by the salts in the solution decreasing the solution resistivity) may have over polarised the lead and anodes, leading to corrosion.

The SCE was recalibrated, the power supply disconnected and the potential of the toilet was measured several times over three weeks (see Table 4) using a SCE at various points around the toilet which gave, as before, slight differences over the whole toilet. During the two weeks that the impressed current cathodic protection system was operating, the lead potential range had decreased from the initial range of 60mV to 40mV. Two weeks after the impressed current had been de-energised (disconnected) the difference in potential range had further decreased to 30mV. After another week the potential range remained at around 30mV. Since the un-corroding toilet had a potential difference of 20mV it was assumed the driving potential between the anodic and cathodic sites on this toilet was now negligible, due to passivation by the cathodic protection. However, it was decided to recommence the cathodic protection because the depolarised potential was returning towards potentials at which the toilet had previously been corroding. It was also thought that the impressed current might set up an ionic gradient across the solution encouraging dissolution of chloride ions into solution.

Table 4: Toilet 124.00010. Potential measured wrt SCE, current off

Date	Timing and type of recording	Maximum potential (mV)	Minimum potential (mV)	Driving emf (mV)
12/2/98	Potential before current applied - corrosion current	-285	-225	60
3/3/98	Immediately after current switched off - off potential	-410	-370	40
17/3/98	After 2 weeks - depolarised potential	-380	-350	30
24/3/98	After 3 weeks – depolarised potential	-374	-343	30

4.3 Cathodic protection method II.

This method follows AS2832.1-2004 Clause 2.2.3. A new system was set up using new electrodes and setting the power supply to current control. 12 anodes were connected in series with a 10□ resistor to the positive terminal. The toilet was connected to the negative terminal with a dry alligator clip as before. The least negative depolarised potential reading of the lead was -343mV wrt SCE (Table 4). For this attempt, current was applied more conservatively to shift the depolarised potential 100mV in the negative direction i.e. to -440mV wrt SCE as per the Australian Standard clause 2.2.3. The results are listed in Table 5.

The system was set up with an applied current of 6.7mA from 2.2 V (see Table 5). A lead on-potential of -500mV gave an immediate off-potential of -415mV. Initially the potential range of on-potentials over the toilet was from -620 to -480mV. Over one month this range gradually increased to -660 to -480mV. The measured outputs were 7.6mA at 2.4V. The current was then increased to 15.6mA to counteract the expected water resistance decrease due to chlorides being extracted from the ceramic, as had happened during the first attempt.

After the next four days the water was crystal clear, whereas previously, small amounts of corrosion or scum had been visible on the water. However after 12 days the anodes had the appearance of beginning to crumble and small specks of metal were visible on the bottom of the tank. On and off-potential measurements were taken and the power was turned off. Off-potential measurements of – 450 to – 400 indicate the standard was being met (as specified in AS2832.1-2004 clause 2.2.3 which requires the off potential readings to be measured), but the range of potentials across the toilet had increased. Chloride levels and pH readings were taken indicating a high pH near the surface of the lead and a low pH near the anodes as expected from the electrolytic decomposition of water.

The toilet was left sitting in the tap water with the impressed current disconnected but after eight days active corrosion began to form over the lead surface. Since the chloride ion concentration was high (51ppm) the solution was replaced with fresh tap water. The anodes were cleaned in HNO_3 and placed back in the tub. The circuit was reconnected using intermediate values of 10mA and 2.9 V. After 14 days a small amount of active corrosion was visible on areas of the lead toilet. There was also a build up of red precipitate on the anodes. It is possible that HPbO- (plumbous ion) had formed in the crevices of the lead where the alkalinity would be highest (Cherry 1994). As a negative ion, this would be attracted to the anodes. Previous XRD results had indicated lead was plating out on the anodes as brown $PbSO_4$ and PbO_2.

The current was decreased to 9.1mA and 2.8 V where the lead appeared to remain stable. An aquarium pump was also added to the system. This was to reduce the build up of high pH near the lead and acidity at the anodes.

After this period potential measurements were not taken regularly but the impressed current and stirrer remained on. The decrease in protection current caused an increase in on-potential and an increase in variation over the toilet. The final on-potential readings ranged from -690 to -500mv wrt SCE – which is comparable to AS2832.1-2004 Clause 2.2.2.4. Because the system was not turned off, there are no further instantaneous off-potentials to compare to Clause 2.2.3. However, previous readings were from -450 to -400, so around 100mV more negative than the depolarised potential of -343mV. It appeared there was not the problem of over-polarisation as had happened in the first attempt, where high chloride concentration had caused breakdown of protective films.

Chloride measurements taken after several months recorded 20ppm near the ceramic and 30ppm near the anodes. This appeared to show that the impressed current might attract negative chloride ions towards the anode, encouraging further release of chloride ions from the ceramic into solution.

Over nine months the tap water was changed twice and the anodes cleaned. Again a high pH was recorded at the metal surface (pH=10) so the aquarium pump was replaced with a more powerful stirrer. This circulated the water slowly but thoroughly. This new stirrer also reduced the amount of scum that was forming on the surface of the water. However minor corrosion was still noted so after 10 months a high-powered pump and stirrer rated for continual use replaced the earlier version.

Over 6.5 years the solution was changed approximately three times/year and the [Cl-] was monitored using an electronic chloride meter with an $Ag/AgCl_2$ electrode until it dropped to 16ppm. The tap water was then replaced with reverse osmosis purified water. No corrosion occurred at this time indicating that the cathodic protection continued to be effective and the polarisation of the lead was maintained. It was possible the lead in solution may have interfered with the chloride meter readings. Therefore, the final [Cl-] measurements were done using ion chromatography (CSIRO, Melbourne). The final desalination took another four months until chloride levels, detected by ion chromatography, gave three consecutive monthly readings of less than 10ppm.

The toilet was then disconnected from the cathodic protection, removed from the tank and air dried. No new corrosion products formed and the lead had a whitish silver appearance (see Figure 7)

Table 5: Measurements taken for toilet 124.00010 during current adjustment to reach stable cathodic protection.

Date 1998	Description	mA	V	On-potential* range wrt SCE /mV	On-Potential* variation/ mV	Off- potential* wrt SCE /mV	Off-potential* variation/ mV	pH	[Cl-] /ppm
9/4	Initial set up	6.7	2.2	-500		-415			
		6.9	2.5	-620 to -480	140				
14/4		7.2	2.6	-644 to -484	160				
20/4		7.0	2.4	-656 to -489	167				
24/4		7.5	2.4						
27/4		7.4	2.4						
4/5		7.5	2.4	-654 to -488	166				
7/5		7.6	2.4	-659 to -480	179				
14/5	Increase current	15.6	3.0	-700 to -500	200				27
15/5		15.5	2.95						
18/5	crystal clear water	15.5	2.85						
19/5		15.5	2.8						
21/5		15.7	2.8						
26/5	anodes crumbling, power off	15.8	2.8	-640 to -440	200	-450 to -400	50		
	Water sample near lead surface							10.4	34
	Water sample near anodes							4.3	34
3/6	active corrosion, power on	10.1	2.9	-620 to -440	180				51
5/6		10.2	2.9						
9/6		10.4	2.95						
10/6		10.4	2.95						
12/6		10.6	2.95	-670 to -485	185				
115/6		10.6	2.95						
17/6	Slight corrosion	10.7	2.95						
	Decreased current	9.1	2.8						
26/6		9.2	2.8	-690 to -500	190				
29/6		9.2	2.8						

* The measurement shown as the "on potential.." is made up of two components being the metal's polarised potential and the potential drop of the current flowing through the water (IR error). The measurement shown as the "off potential...." indicates the metal's polarised potential excluding the IR error and is the potential against which the level of protection is measured.

Figure 7 – Toilet 124.00010 After Treatment

5. Discussion

Toilet 124.00010 was desalinated using impressed current cathodic protection, initially following guidelines in AS2832.1-2004 Clause 2.2.2.4. An on potential level of -530mV wrt SCE reference electrode was achieved on the toilet with the system under voltage control. This depressed the original depolarised potential by 305mV i.e. similar to that recommended by Pourbaix (1974). However, after 12 days active corrosion was visible over the lead toilet and the anodes were crumbling. It is thought the continued desalination of the ceramic increased the chloride and other ion levels, and this increased the conductivity of the system. This caused an increase in current and possibly over-polarisation of the lead and anodes. pH changes from the electrolytic decomposition of water may have had an influence but pH measurements taken from near the anodes and cathode do not support this. A second attempt was made, following AS2832.1-2004 Clause 2.2.3. This recommended a potential almost 100mV more negative than the depolarised potential, in this case –343mV. Aiming for an instantaneous off-potential of -440mV, we found that an off potential level across the toilet of -400 to -450 mV wrt SCE achieved effective cathodic protection with the system under current control. Increasing the current produced the beginnings of corrosion so it was reduced. This corresponded to an on-potential of -500mV wrt SCE and a depolarised potential shift of -157mV. AS2832.1-2004 recommends -574mV wrt SCE or a depolarised potential shift of -100mV to cathodically protect buried lead. No standards are available for immersed lead but Pourbaix (1974) suggests that the potential of the lead be lowered to below about -0.3V. Our results show that for historic artefacts at least, published recommendations should be used as a guide and that trial and error methodology continues to be necessary.

Measurements throughout the second attempt (following AS2832.1-2004 Clause 2 .2.3) indicated a high pH near the lead and a low pH near the anodes as expected from the electrolytic decomposition of water. A water stirrer and pump was added to increase diffusion. When a powerful mixer with the capacity to agitate all the water in the tank was introduced, the remaining corrosion ceased and the cathodic protection became effective. The toilet remained in this configuration for four and a half years. The tap water was changed about three times/year. In the last year of treatment the tap water was replaced by purified (reverse osmosis) water and the cathodic protection continued to be effective.

We considered the possibility that aerated stirring of the water without the use of cathodic protection may have been sufficient to increase CO_2 levels and protect the lead. The presence of dissolved carbon dioxide can form insoluble protective $PbCO_3$, (Cerussite), which can passivate lead between pH 5 - 12 (Bordass, 1998). Similarly, it was not clear if leaving more of the carbonate concretions on the lead surface could have protected the lead by producing protective carbonates. However because of the negative LSI of the water the formation of $PbCO_3$ may not have been favoured. Rather, the lack of a continuous layer may have favoured the development of corrosion cells. Therefore due to the lack of knowledge and information on these complex corrosion mechanisms it was felt that applying cathodic protection remained the most appropriate action.

During the treatment, regular readings of the concentration of chlorides were taken. Readings indicating higher [Cl-] near the anodes than near the toilet appeared to confirm that chlorides released by the ceramic were being attracted to the anodes and away from the ceramic. The toilet took an unexpectedly long time (6.5 years) to fully desalinate to the required level. Usually an earthenware object of this size would be expected to take 1 or 2.5 years to desalinate. However, the underside of the ceramic was covered in lead so all chloride ions had to pass through the glazed external face.

Once the chloride readings were at an acceptable level the toilet was removed from the tank and allowed to air dry. No new corrosion products formed during this process.

When the object was dry, different light and dark grey bands across the lead became visible. The bowl was pale grey while the down pipe had two dark and one light coloured area. There was a small amount of pitting visible on the lead in the upper light coloured area of the lead area (around the bowl). Interestingly, the darker coloured areas of lead had not corroded indicating that different lead compositions on the toilet may have played a part in the lead corrosion. This supports the assumption that differing lead compositions within the toilet may have set up corrosion cells.

While there was a small amount of pitting visible on the lead in the upper light coloured bowl area, the ceramic was in excellent condition following this treatment and 1.5 years after completion does not show any evidence of deterioration caused by soluble salts.

6. Conclusions

A lead and ceramic toilet recovered from a maritime archaeological site was desalinated with the aid of impressed current cathodic protection to limit corrosion of the lead. Although some corrosion of the lead occurred during the initial set-up period, this was minimised with the impressed current cathodic protection system. A protection current was applied to shift the on-potential 150mV in the negative direction from the depolarised potential. The level of applied current is a determining factor and was applied as low as possible, however it could increase with increasing levels of dissolved salts in the tank. Australian Standards and Pourbaix (1974) provided some guidelines to determining the size of the potential shift needed; however the successful protection potential had to be found by trial and error. Thorough, continuous stirring to neutralise the electrolyte at the anode and cathode was an essential part of the treatment. The desalination treatment of the ceramic was completed successfully after 6.5 years of treatment and the ceramic is in excellent condition (Figure 7).

This was a complex and time consuming treatment not helped by the treatment being continued by six different contract staff, and lack of funding to conduct extensive analysis. Disassembly of the composite object could have avoided the need for cathodic protection but this was considered too high a risk for such a significant object. The lack of practical experience with cathodic protection on the part of the conservators (now rectified thanks to this treatment) may also have introduced some delays. While there was a small amount of pitting visible on the lead in the upper light coloured bowl area, the ceramic was in excellent condition and does not show any evidence of deterioration caused by soluble salts, even 1.5 years after the completion of the treatment. It was placed on display for nine months in 2004.

We hope that by discussing both the setbacks and successes of this treatment, we have illuminated some of the complexities of the conservation of such complex, composite, archaeological objects.

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Antarctic Observations: On metal corrosion at three historic huts on Ross Island

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Abstract

A range of commercial and standard corrosion inhibitors and coating systems were applied on-site or off-site onto a variety of metal artefacts and coupons and exposed to ambient conditions in three historic huts: Discovery Hut, Cape Evans and Cape Royds on Ross Island in Antarctica. Qualitative observations regarding the efficacy of these treatments has been made over a seven year period of exposure trials and these observations are compared with environmental data collected in the huts during that same period. The aim of this research was to significantly improve our qualitative understanding of the local corrosion phenomena and to answer the question "Is it feasible in the Antarctic summer period, to develop a tailored and effective on-site metals conservation program for artefacts in these historic huts?"

Keywords: Antarctica, corrosion, corrosion inhibitors, protection, coating, on-site treatment, observations,

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1. Introduction

The Antarctic Heritage Trust (AHT) is based in Christchurch, New Zealand and was formed in 1987 to "preserve and protect the physical and historic heritage of human endeavour in Antarctica". Antarctic heritage primarily revolves around the heroic era of Antarctic exploration which includes "documented feats of scientific achievement, exploration and endurance" (Antarctic Heritage Trust ,2004) .

Under the auspices of the AHT a field event supported by Antarctica New Zealand titled K282 was sent seasonally to Ross Island in Antarctica to carry out conservation work primarily on the historic huts and their associated artefact assemblages.

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The huts were built by Borchgrevink, Shackleton and Scott's two expeditions.

The huts in order of erection are:

- Cape Adare in Northern Victoria Land (British Southern Cross Expedition 1898 -1900 led by Carsten Borchgrevink)
- Discovery Hut at Hut Point (Figure 1) (National Antarctic Expedition 1901 – 1904, led by Commander RF Scott)
- Nimrod Hut at Cape Royds (Figure 2)(British Antarctic (Nimrod) Expedition 1907 – 1909 led by Ernest Shackleton)
- Terra Nova Hut at Cape Evans (Figure 3) (British Antarctic Expedition 1910 – 1913 led by Captain R F Scott) (Antarctic Heritage Trust ,2004) .

Figure 1: View of Discovery Hut at Hut Point, National Antarctic Expedition 1901 – 1904, led by Commander RF Scott.

Figure 2: View of Nimrod Hut at Cape Royds British Antarctic (Nimrod) Expedition 1907 – 1909 led by Ernest Shackleton

Cape Adare is logistically the most problematic to reach and only periodically is visited by members of AHT.

Figure 3: View of Terra Nova Hut at Cape Evans, British Antarctic Expedition 1910 – 1913 led by Captain R F Scott.

Since the huts "rediscovery" in 1946 during the U.S. Navy launched *Operation Highjump* led by Rear Admiral Richard E. Byrd, loss of artefacts around the historic sites has accelerated due to a combination of environmental and human factors.

Each site has three basic components: the hut structure, artefacts inside, artefacts and small structures outside. This paper will address qualitative experimentation undertaken to better ascertain a conservation approach for the internal artefact assemblages. Preventive conservation is vitally required in all circumstances where the artefacts remain in situ; consequently the various merits of on-site versus off-site interventive conservation were assessed.

The Huts are all wooden structures located near the Ross Sea. Each hut is unique in its orientation, susceptibility to prevailing conditions and range of internal microclimates. A general approach to the huts by the NZ Antarctic Society began in 1960-1961 season at Cape Royds and Cape Evans. This was followed in 1963-1964 at Hut Point. Each hut was excavated to remove built up ice. Following the ice removal, hut structures were stabilised and weatherproofed resulting in the drying out of the internal environment.

In 1997 research was initiated to assess the potential of developing a tailored conservation approach for the internal artefact assemblage that could be effectively delivered during the summer period. Metal artefacts of particular significance for AHT were the range of historical food stuff cans that still have contents and labels (Figure 4). Sampling of internal metal objects was conducted to develop a baseline appreciation of the corrosion phenomena at each site and to determine the range and extent of chloride ions within the internal artefact assemblage. This program was conducted over six field seasons in the last seven year period.

Figure 4: An internal wall of packing cases filled with cans and bottles at Cape Evans.

1.1 Bumped, bounced or boomeranged

One important element to comprehend in regards to fieldwork in Antarctica is the simple logistical difficulties faced in getting to and from Antarctica and to and from the site. Antarctica New Zealand is able to coordinate flights to Antarctica with the US or Royal New Zealand Air Force. If you are fortunate to fly to Antarctica rather than sail for several weeks, the trip is still made problematic by the fact that you can be bumped, bounced or boomeranged. Travel to the ice is heavily weather dependant and also based on event priorities and status of travellers at times. Bumped means that your flight is cancelled for what ever reason and you may leave the next day. Bounced is when you have been in line for two to three hours, have handed in all your luggage, are dressed in full survival gear during summer and then told you are not flying that day and to go back to your accommodation. Boomeranged is where you have even managed to fly some or practically the whole 8-9 hours of the trip to Ross Island and then are forced to return to your point of departure to try again the next day.

Once on the ice where your event is reliant on helicopter access to get to sites, you are once again subject to the full array of possibilities and weather dependency. If you are very early in the season you can travel to the historic huts of Cape Evans and Royds by tracked vehicle. Hut Point is practically always accessible from Scott Base by car or foot.

2. Experimental methods

2.1 Temperature and relative humidity data

Temperature and relative humidity data for the three huts was acquired hourly for two years using HOBO® H8 Pro data loggers by National Science Foundation event number BO-038-0 and New Zealand event K021, as part of an ongoing study of the biological deterioration of the huts (Held et al 2003, Blanchette et al 2002, Blanchette et al 2004, Held et al 2004). The loggers were downloaded annually in 2001 and 2002 by team members. The number of data loggers used in Discovery Hut, Cape Evans and Cape Royds are 4,6,5 respectively. The data loggers were distributed throughout the huts internally at varying points and heights and also located outside (Held et al 2003. Held et al 2004).

2.2 Coupon experimentation

2.2.1 Coupon Dimensions and Attachment

Two types of coupons were used in experiments:

- Traditional bronze coupons cast at the Roman Art Foundry in Epping, Victoria with metallurgy of 85% Cu, 5.5% Pb, 4.2% Sn and 5.3% Zn. The cast size for bronze coupons was 80 mm x 80 mm x 6 mm.
- Mild steel coupons complying with BHP AS/NZS 3678 – 250 structural steel plate. The maximum composition data for BHP structural steel plate is; C: 0.22, Mn: 1.70, P: 0.04, Si: 0.35, S: 0.035, A: 1.00. The mild steel coupons were 8 mm x 7.5 mm x 5 mm.

Mild steel coupons exposed in 1996 were clean faced. All coupons exposed in 1999 and again in 2001 were prepared to 400 grit using a polyurethane lap. A hole (5 mm) was drilled near one edge in the middle of each coupon to facilitate their being suspended using synthetic thread.

2.2.2 Coupon preparation

A range of commercial and standard corrosion inhibitors and coating systems were brush applied on-site or off-site, in controlled environmental conditions onto a variety of metal artefacts and coupons. They were exposed to ambient conditions in three historic huts: Discovery Hut, Cape Evans and Cape Royds on Ross Island in Antarctica. The brush method of application was chosen as it is the most useable method in the field for working on artefacts. All coupons were degreased with acetone and air-dried before coatings were applied.

2.2.3 Coupon Exposure Dates

All mild steel coupons were exposed inside the hut at Cape Evans suspended under the bed frames in Dimitri and Anton's bunk area. The copper coupons were placed in 2001 on the upper shelf between the Biology area and Nelson and Day's bunk (Figure 5).

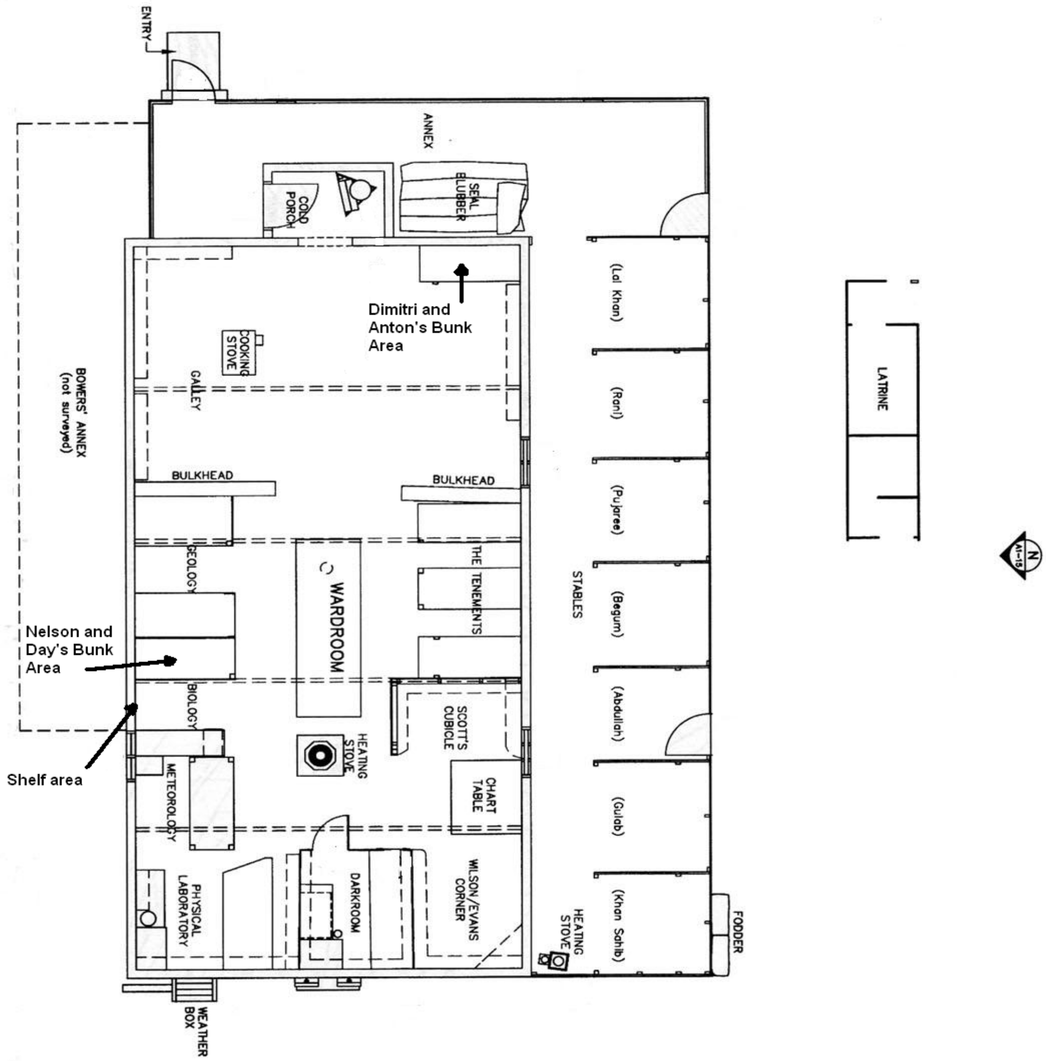

Figure 5: Location of coupons exposed inside the hut at Cape Evans suspended under the bed frames in Dimitri and Anton's bunk area and on the shelf between the biology area and Nelson and Day's bunk area. Interior plan from JASMAX Architects, 65 Upper Queen St, Box 6648, Auckland, New Zealand.

Three exposure trials were undertaken. The first trial was for approximately a three year exposure period (November 1996 –December 1999). Mild steel coupons were coated with Galmet Ironize, Dinitrol AV8, Rusticide, microcrystalline wax, Ferro Guard F.S. Grease and or combinations of the above (Maxwell, 1998).

The second trial was for approximately a one year period (December 1999 - January 2001). Coupons were mild steel, coated with Rust Stabiliser M.D.P., Preservation Wax 400, Dinitrol 4010, Tectyl 506 and ARI(Maxwell, 1999). .

The third coating trial was also for approximately a one year period (January 2001 – January 2002). Copper and mild steel coupons were coated with ARI or Besq 195 a microcrystalline wax (Viduka 2001,. Viduka 2002)

2.3 Artefacts off-site treatment

Ten iron alloy objects from the laboratory at Cape Evans located in the South East Wall area of the Hut were removed and conserved off-site by Lynn Campbell and Karel Peters, conservators then based in New Zealand working for the Trust. The objects were all treated with 10% citric acid, an inhibitor being 1% potassium chromate, or corrosion converter 3% tannic acid and a wax coating. Objects were relocated in 1987 to their previous locations inside the hut at Cape Evans and exposed to internal ambient conditions.

In 1997 nine objects were removed for off-site treatment as they represented the range of metal and metal alloys present inside the hut at Cape Royds. Their surface conditions varied from poor to very poor. This terminology related to the state of corrosion. Poor was a corroded surface with a mixture of stable and unstable corrosion salts, and very poor being a surface consisting of all active corrosion and mechanical damage/losses to the object. The objects consisted of:

Object	**Material**	**Conservation Treatment**
1. Enamel pie dish – small	Iron base alloy	Galmet (conversion coating/lacquer)
2. Enamel pie dish – large	Iron base alloy	Galmet (conversion coating/lacquer)
3. Shelf bracket – small	Iron base alloy	Rusticide plus Ferroguard FS
4. Shelf bracket – large	Iron base alloy	Rusticide plus Dinatrol 4010
5. Iron bolt	Iron base alloy	Rusticide plus Tectyl 506
6. Tube valve	Zinc/copper base alloy	2 coats of Ferroguard FS
7. Zinc pulley casing	Zinc base alloy	2 coats of Ferroguard FS
8. Copper tube	Copper	3% Benzotriazole (BTA) plus microcrystalline wax
9. Oil tin	Tinned, iron alloy, brass & leather	3% Phosphoric acid plus 2 coats Ferroguard FS

Table 1: Objects, material and conservation treatment applied. (Data on coating and inhibitors available in materials and supplies section.)

All objects were initially treated to remove free corrosion salts as follows:
1. Loose corrosion products were removed by lightly brushing with a soft paint brush
2. Objects (except no. 9) were then washed for 24 hours in a bath of water and 2.5% non ionic detergent (Lissapol)
3. After removal from the bath and drying with ethanol, the objects were left for 48 hours exposed to the air indoors in a non air conditioned environment. This timing allowed for redevelopment of any corrosion products

After the initial washing and cleaning processes the objects were treated using a range of standard conservation and commercial products (Table 1). The aim of applying a variety of treatments was:
1. to establish suitable treatments for stabilisation of corroded metal
2. Analyse corrosion salts to determine the extent or pattern of the corrosion salts present and suitability of treatments for field testing
3. Investigate the feasibility of applying those treatments at Scott Base or in the field

Objects were all returned to their previous locations within the hut at Cape Royds during the 1998-9 season (Maxwell, 1999).

2.4 Artefacts - on-site treatment experimentation

2.4.1 Metals

The methodology to treat objects on-site was constrained by two factors;

- Environmental conservation and workplace regulations that restrict the types of materials that can be taken to Antarctica,
- the ambient conditions during the summer months that further limited product choice.

In 1998-1999, on-site treatments were performed on a series of artefacts that included cans with labels and contents, bed frames and the stove at Cape Royds. The artefacts were coated by brush application using either halogen lights to heat the metal surface before application, or directly onto the surface. A coating or coatings were applied until a smooth even coat was observed (Maxwell, 1999).

The coating product used on-site now trades as ACTIVE RUST INHIBITOR GP3000 (ARI) but in 1998 was still in its early developmental phases. ARI was trialled because it complied with the existing Antarctic constraints and whilst problematic to apply in the ambient conditions, it is suitable to be transported by air, is removable with caustic solution and offered several advantages over other then commercially available products.

The ARI coating is a water-based emulsion of non-toxic polymers incorporating corrosion inhibitors of low odour. On application the product produces a hydrophobic film that is not easily displaced or penetrated by water and does not alter the surface appearance significantly. According to Gerald Cairns, senior chemist at Cairns Corporation, when ARI GP 3000 is “applied to oxidised metal surfaces, especially rusty steel surfaces, it partially dissolves the upper oxide layers and carries this down into the interstices in the underlying rust then penetrates to the parent metal surface where it reacts to form a tight bond. The oxide layer tends to flatten out under this influence. Thus the whole oxide layer becomes a hydrophobic protective coating without altering the surface appearance significantly. The amounts of oxides present determine how much needs to be applied either by way of dilution rate or multiple coats” (Cairns 2000).

2.4.2 Paper experimentation

A series of panels of acid-free paper were coated with a range of concentrations of ARI and water: pure ARI, 1:1, 1:2, 1:3 and left in the dark in Shackleton’s room to be seasonally assessed for colour change against a blank (Figure 6) (Viduka 2002).

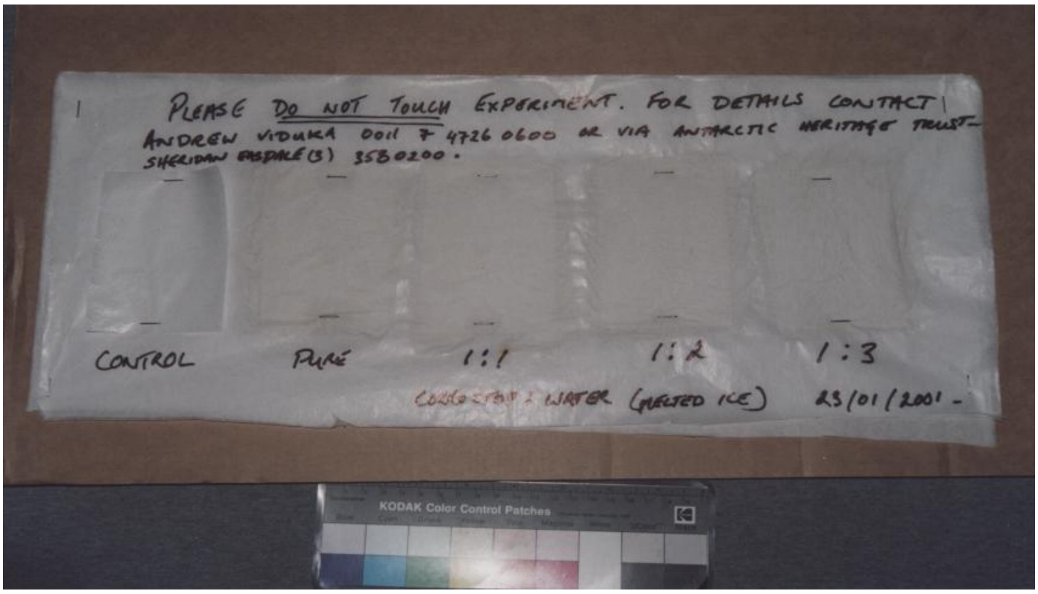

Figure 6: Simple experiment to monitor the effects of ARI on paper.

3. Results and Discussion

3.1 The Corrosive Environment

Observations made over the years by the authors have borne out several now well documented facts (Held 2003, Maxwell 1998, Viduka 2001) Each site is not uniformly corrosive and prevailing conditions and site layout can be used to comprehend the topography of deterioration. The primary driving mechanisms for the deterioration of the outside and inside artefact assemblages are different. Outside artefacts are exposed to a combination of:

- high wind's [that can collect scoria dust and physically scour the surface (Figure 7)]
- high UV causing bleaching of organic materials
- significant concentrations of corrosive salts in the soil and in the snow and ice that on Ross Island can form thin crusts on the surface of the soil (Campbell and Claridge 1987)
- aerosol salt solutions from the Ross Sea
- the summer period when temperatures rise above freezing allowing snow to turn into melt water and increases rate and extent of fluctuating Relative Humidity

For inorganic objects the proximity to dissimilar metals, the location of snow banks, run off channels, melt water drip lines and exposure to prevailing weather conditions do cause accelerated rates of corrosion. The presence of free water condensing onto cold metal surfaces is enough to start cyclic corrosion (Figure 8) and is compounded by the presence of corrosive salts present in ice, snow and air.
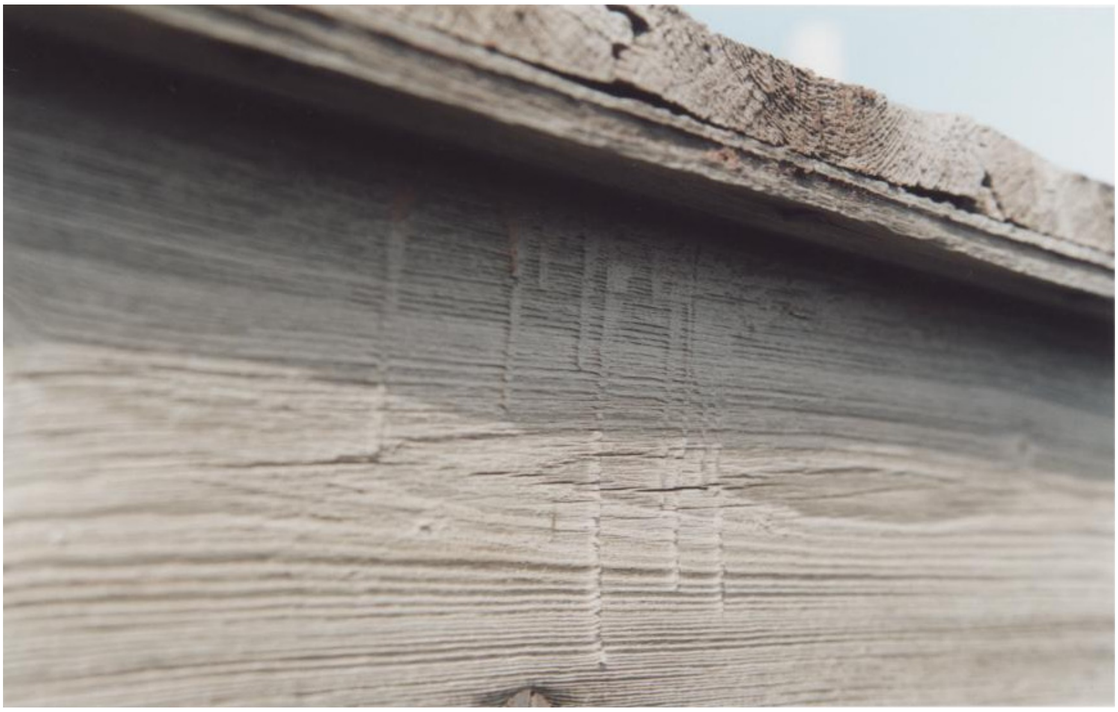
Figure 7: Early wood has been removed by wind ablation on Discovery Hut leaving late wood in pronounced ridges. Note paint drip lines afforded longer protection leaving a last vestige of the original surface.

Figure 8: Active corrosion on can (Reserve Collection Scott Base)

The rate of chemical deterioration is constrained by the shortness of the summer period after which objects located outside are in the majority of instances, covered by snow or ice. Analysis of iron corrosion products from objects inside and outside the huts has identified Goethite as a common corrosion product (Tilbrooke, 1998.). This mineral salt is formed in low temperatures and low humidity indicating that corrosion, whilst at a slower rate, still does commonly occur outside the summer period (Viduka 2002, Deer 1966).

3.1.2 Inside Objects

Analysis of corrosion product samples collected by Maxwell in 1997 - 1998, 1998 -1999 seasons was analysed using semi-micro qualitative wet chemical methods to determine the anions and cations present and to allow an estimate of their concentration levels in the sample (Viduka 2002).The analysis was conducted by David Tilbrooke of Museum Environment and Conservation Services based in South Australia. Results from the analysis indicated that inside artefacts were found to be generally free of chlorides ions. These objects were observably in better condition than similar objects located outside. Some inside artefacts have higher concentrations of chloride ions than others, but this may indicate previous collection management practices rather than differentiated exposure inside a hut. David Harrowfield (a leading Antarctic historian) confirms that artefacts have been recovered and brought back into the huts subsequent to the huts excavation from the ice (Harrowfield 2000.).

For objects located inside the huts, the instigating mechanisms of corrosion are:

- Actual amount of water vapour present at low temperatures and associated with high RH (Figures 9, 10,11,12). (Viduka 2002)
- Presence of free water condensing onto cold metal surfaces
- Proximity of the object to the floor or external walls
- Lack of air circulation around objects
- Proximity of dissimilar objects to each other

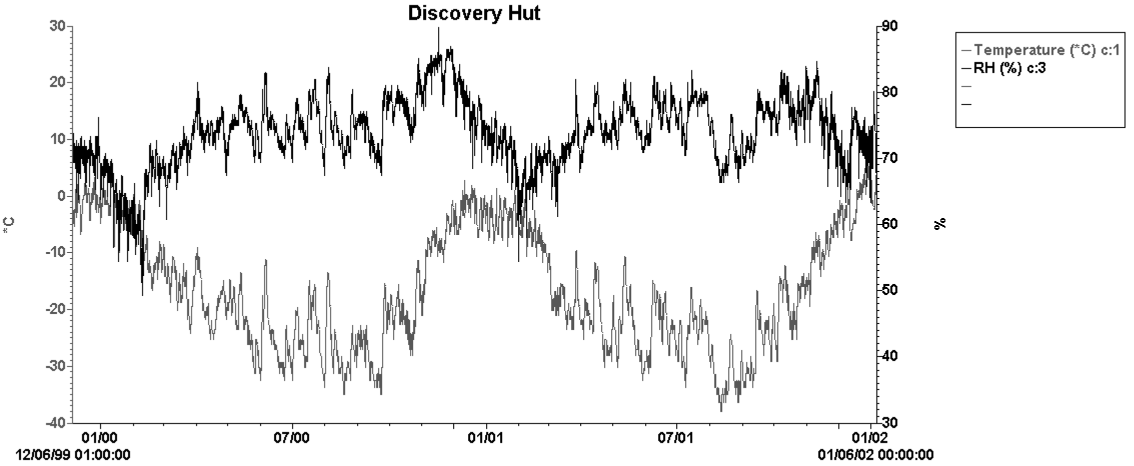

Figure 9: Graph of relative humidity and temperature in *Discovery* hut over a 2 year period (Held *et al* 2003).

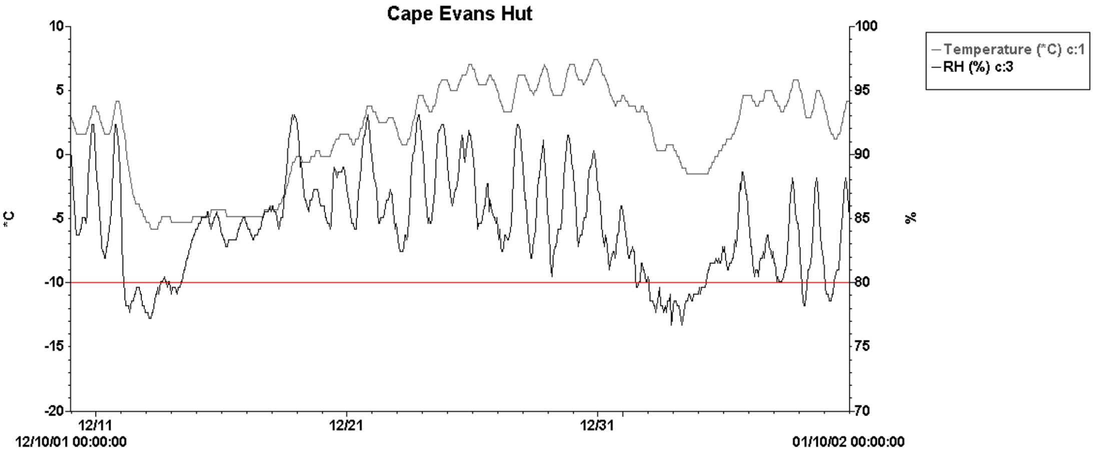

Figure 10: Graph showing relative humidity and temperature in Cape Evans hut over a one month period indicating high relative humidity and temperatures above 0ºC. The horizontal line indicates 80% relative humidity (Held *et al* 2003).

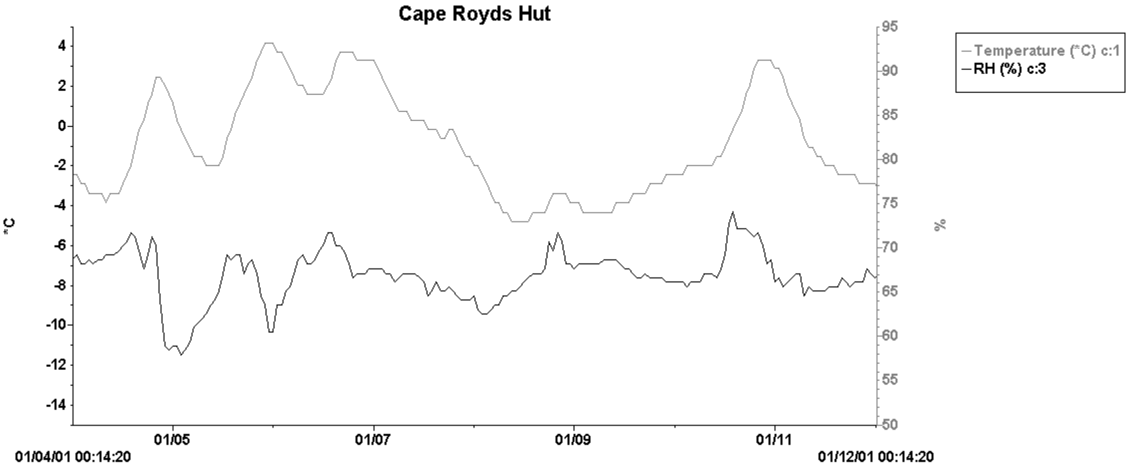

Figure 11: Graph of relative humidity and temperature in Cape Royds hut. The vertical line indicates a day in which 66 visitors entered the hut (Held *et al* 2003).

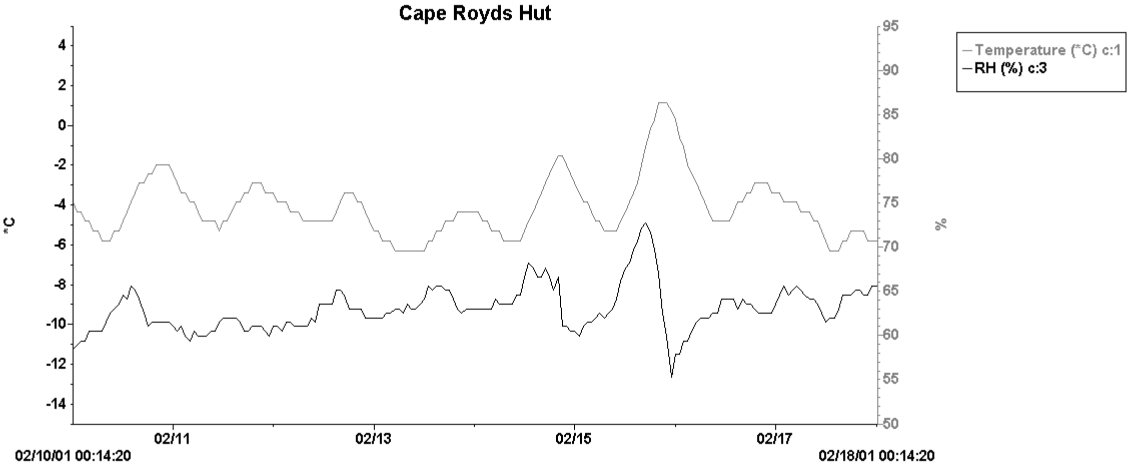

Figure 12: Graph of relative humidity and temperature in Cape Royds hut. The vertical line indicates one day in which 45 visitors entered the hut (Held *et al* 2003).

Corrosion on objects inside the huts is typically cyclic pitting corrosion developing to sheet like corrosion. Inside the huts biological deterioration is present in the form of soft rot of timbers, surface moulds on wood, leather, foodstuffs and other artefacts indicative of the availability of water in the closed system. Held writes, "Fungal growth is most common on wood near or on the floor and often in areas with limited air circulation" (Held *et al* 2003) . Equally, metal corrosion is most extensive in similar physical locations as there is more available water and greater temperature extremes.

Environmental data acquired from the huts reveal that in summer, temperatures rise above freezing, and relative humidity (elevated for most of the year) is often over 80%. Data from Discovery Hut shows the relationship of RH and temperature over time. RH is quite elevated though temperature only rises above freezing for short periods in summer (Figure 9). Data collected at Cape Evans over one month from December-January 2002 shows RH at 85% up to a maximum of 93%, average temperature for the period is 1.4^{0}C and reaches a maximum of 7^{0}C. These conditions are conducive to forming corrosion cells and mould growth within the hut (Figure 10) (Held 2003).

3.2 Coupon experimentation

3.2.1 November 1996 - December 1999 coupon trial

Coupons were coated with: Galmet Ironize, Dinitrol AV8, Rusticide, microcrystalline wax, Ferro Guard F.S. Grease and or combinations of the above. Results of the exposure trials were that only those coupons coated with lacquers did not fail and start corroding. All wax coatings used in the study broke down.
The results from the study indicated:

- the extreme internal corrosive environment an object faces when located on the floor or near an outside wall
- that preventive conservation should be prioritised in those areas that are subject to extreme damp and cold.
- that water access to the metal surface must be totally stopped to inhibit corrosion within the inside environment
- that the difference in micro-environments within a hut is extreme.

The last observation is borne out by comparative observation with Karel Peter's stripped and wax coated objects located high up on a shelf in the South East wall area. Eight of the original ten objects treated in 1987 were still stable and showed no sign of re-corrosion in 2004 [15].

3.2.2 December 1999 – January 2001 coupon trial

The coupons were coated with: Rust Stabiliser MDB, Preservation Wax 400, Dinitrol 4010, Tectyl 500 and ARI developmental formula and exposed internally for one year after which there was no visible signs of recorrosion. The coupons coated with Tectyl 500 were still sticky to the touch. The length of exposure was insufficient to make observations regarding the long term performance or suitability of these products.

3.2.3 January 2001 – January 2002 coupon trial

The third coupon based experiment focussed on the potentially most environmentally friendly commercial product ARI and was expanded to include copper coupons for comparative purposes. Previous Electrochemical Impedance Spectroscopy (EIS) studies conducted in Australia on the ageing properties and corrosion resistance of protective wax coatings on metal surfaces, found TWA2095 a microcrystalline wax, offered the best long term corrosion resistance of a group of commercial preparations including BeSq 195, Cor-Trol 400, Cor-Trol 450, Dinitrol AV100, Dinitrol AV25 and Dinitrol 4010 (Otieno-Alego et al 2000, Otieno-Alego et al 1998) When TWA 2095 became difficult to acquire in Australia, BeSq195, another micro-crystalline wax, was identified as the best commercial replacement. Even though waxes were found ineffective in the first trial, the rationale for Besq 195's inclusion in this trial was the belief that this wax might survive and offer a performance baseline against the 2000 ARI formula, giving meaningful comparative results when studied post exposure using EIS.

Observations made during application (Viduka 2001) noted that the ARI coating formula did not apply evenly, and that spots of flash rusting occurred almost immediately on some objects. Subsequent to the field season this issue was investigated further and the Cairns Corporation identified a phase separation problem in the 2000 ARI formula. The stoichiometry of the formula was subsequently changed to remedy this, immediately invalidating the exposure trials.

During the 2001-2002 field season the coupons were visually assessed on-site and the ARI formula was found to have universally not inhibited corrosion. The coupons exhibited streaky corrosion lines associated with phase separation, while the BeSq 195 gave uniform protection. Besq 195 was not subsequently studied using EIS due to logistic and equipment difficulties at the time.

3.3 Artefacts off-site treatment

Of the nineteen artefacts that had been removed and treated off-site using various standard conservation or commercial treatments, by 2004 only two of these objects had started to show active corrosion and these two were from the earlier 1987 treatment batch. The 1987 treatments were essentially a strip, inhibit and wax coat process. The only variable between the two objects that are corroding is that a different solution was used, one had tannic acid conversion and the other potassium chromate inhibition, and both were waxed coated.

Since conservation is not a one off process and the object's environment is not conducive to long term storage, the recorrosion of some artefacts is not surprising. But why have the other objects survived so well? Certainly the artefacts that have been treated have not been located in any of the more aggressive internal micro-environments, and this fact combined with effective conservation treatments may explain the continuing stability of the remaining seventeen artefacts.

3.4 Artefacts on-site treatment experimentation

3.4.1 Metals

Prior to departure for the 2001-2002 field season the Cairns Corporation supplied a new batch of ARI to be used in the field. Since no coupons were prepared for that year, three cast iron bed frames at Cape Evans and two food cans with contents at Cape Royds were approved to be included in the artefact experiment trials. The beds were Atkinson's, Oates' and Cherry-Garrard's and the two cans contained boiled mutton and had labels in situ. The beds and cans were coated with a 2:1 solution of ARI:water. Bickersteth and Clendon who went to the ice with K440 in 2004, report that the condition of these bed frames appears stable with no observable active corrosion. The two cans of boiled mutton were tacky to the touch, glossy on the outside, but matt near the seams. Active corrosion was evident, particularly on one can (Clendon and Bickersteth 2004).

3.4.2 Observations of GP300 Active Rust Inhibitor (ARI)

All the promise of ARI has not been fully realised within the studies so far conducted. Ongoing product development coupled with regular formula changes has resulted in much effort for little useable return. Practical experience with ARI has taught that the product can require a variable number of coating applications depending on the degree of surface corrosion and the formula of the solution. The changing formula during the development phase meant that some product batches separated in the container and this contributed to uneven and flawed coatings that for a period not only allowed recorrosion but potentially accelerated the phenomena. Subsequent re-application was required to obtain good coating distribution.

Unfortunately all the questions initially posed for this product have not been answered, since each new formula has fundamentally changed the characteristics of the product. The effectiveness of ARI can only be ascertained once the product's development is completed and this is not yet foreseeable.

3.4.3 Paper

Since one of the rationales for trialling ARI was its potential suitability to consolidate both a corroded can body as well as a can's label *in situ*, the effects of ARI on paper alone were trialled at Cape Royds in 2001 with a range of concentrations applied to acid free paper. This paper experiment was observed as recently as February 2004 and at that time, no deterioration, yellowing or staining of the paper swatches coated with ARI had occurred (Clendon and Bickersteth 2004).

3.5 Observations of object treatment off-site versus on-site

Off-site conservation and replacement has been an effective model for the treatment of a very small number of selected artefacts. Difficulties in packing and transport from the ice were circumvented by a careful choice of artefacts. Observations conducted annually since 1997 have shown that Karel Peter's 1987 objects returned to Cape Evans and Peter Maxwell's 1998 objects returned to Cape Royds, post off-site treatment, have remained predominantly stable with only two artefacts recorroding. This statement is subject to one very important caveat: none of these returned objects were relocated in a high risk microenvironment.

In situ interventive experimentation which included treatment applications on corroding artefacts has had mixed results. Prior to 1997 commercial products were applied to artefacts if a treatment was considered required. The most significant example of this was a polyurethane coating applied to the stove at Cape Royds.

Since significant issues regarding the transport and use of commercial products in Antarctica exist, ARI was trialled as an alternative product during its developmental phases. The subsequent difficulties with ARI have been previously outlined and no baseline for comparative purposes was ever established. Best applications of ARI were achieved when halogen lamps were shone onto the metal surface, warming the environment and object surface. The re-treatment done at the rear of the Cape Royds stove in 2000 best exemplifies the effectiveness of this method. Applications of any water borne products generally are applied above 10 ^{o}C for maximum performance.

On the whole, *in situ* conservation is seriously constrained by the simple logistics of working in Antarctic conditions and complying with Antarctic environmental requirements. It would be bold to put forward a view that an effective interventive conservation program encompassing all artefacts could be conducted within the existing framework of camping on the ice.

4. Conclusions

In regards to the conservation of outside objects, the current conditions and technology is such that no viable metal conservation treatment program can be conducted. Some preventive conservation work may be suitable for a portion of this collection. The universal presence of chloride ions both as an aerosol or as salts in the earth and ice, combined with the effects of wind ablation and moisture availability are usually beyond any control.

Observations inside the huts, supported by the environmental data collected by Held *et al* 2003, stress the importance of recognizing the effects of variation in environmental conditions between the huts and within each hut when trying to preserve or prioritise the preventive or interventive conservation needs of interior artefacts. Artefacts located near the floor or outside walls have significantly increased rates of deterioration associated with greater moisture availability.

During summer the RH is high and the temperature is above freezing. The potential and rate of corrosion activity is consequently much higher, and a focus on reducing the RH within the huts during these periods should result in a significant reduction in general corrosion rates and a universally more beneficial environment for the interior artefact assemblage. It does appear from data acquired by Held *et al* 2003 that visitor numbers to the huts have no significant impact on RH inside the huts.

The major process of deterioration for metals inside the huts has been observed to be one of cyclic corrosion, developing from pitting to sheet like corrosion. Obviously the presence of chloride ions will further accelerate this process on a case by case basis. Results from sampling and analysis show that the presence of chloride ions is far from universal within the inside artefact assemblages.

A full range of conservation practices is not recommended for all objects. Some objects inside the hut have not been exposed to the outside environment or damp areas inside the hut and are not assessed as either significant or iconic. Objects which were located outside the hut prior to 1960, and that have been brought inside because of their significance, have a range of conditions.

The challenge put forward by the AHT is to preserve the large number of food cans in the collection, where conditions vary from pristine to very poor. Treating objects off-site has been mainly successful, however, the treatment of this wide range of objects is a costly and slow exercise. In the authors' view it is currently only possible to treat metal objects effectively off-site in a controlled environment, on-site activities should be restricted to preventive conservation only. For the long term conservation of the collection *in situ* the challenge is to stabilise the interior of the huts, and minimise the effects of relative humidity in summer.

Acknowledgements

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Materials and suppliers

Galmet Ionize A rust converter and sealer consisting of resin vinyl/vinylidene Chloride acrylic copolymer. ITW Polymers & Fluids. 100 Hassall Street, Wetherill Park, NSW, 2164 Australia.Tel: (02) 9757 8800 Fax: (02) 9757 3855

Dinitrol AV8 sulfonate corrosion inhibiting compound in an aliphatic hydrocarbon base Gibson Chemical Industries. 138 Kingston Road, Underwood QLD 4119.Tel: (07) 3208 9333 Fax: (07) 3808 4865.

Dinitrol 4010 A high temperature polyester modified wax dispersed with inhibitors Gibson Chemical Industries. 138 Kingston Road, Underwood QLD 4119.Tel: (07) 3208 9333 Fax: (07) 3808 4865

Ferroguard Full Spectrum A solution of vinyl copolymers and organic corrosion inhibitors in an isopropanol base Senson Technology Pty Ltd Unit 1/69 Division Street, Welshpool, Western Australia, 6106.Tel: 61-8-9358 3388 Fax: 61-8-9358 3390

Valvoline "Tectyl 506" A wax emulsion with inhibitors present. Automotive outlets, e.g. Bumper to Bumper, AutoBarn, Thompsons

Active Rust Inhibitor GP3000 (ARI) A water based polymer inhibiting product which has excellent properties to maintain an "as found" appearance. Cairns Corporation Pty Ltd, 221 Brisbane Street, Ipswich, QLD 4306. Tel: (07) 5426 7285 Fax: (07) 5426 7589

Rusticide A tannic/oxalic acid product used for converting active rust to a stable surface. Finish is matt black, but requires overcoating to give maximum performance. A water based product. Flo-Kleen Products, 216 Balcatta Road, Balcatta, WA 6021. Tel: (08) 9345 3122

Rust Stabiliser M.D.P. A moisture displacing pretreatment containing rust stabilizing pigments, synthetic waxes, mineral oils and white spirit solvent. Corroless Automotive Pty Ltd 27 Birubi Street, Cooparoo, Qld 4151. Tel: (07) 3394 3299

Preservation Wax 400 (Now trading as Corroless 400B reinforced wax). A solvent based wax and corrosion inhibitor composition with inert pigment. Corroless Automotive Pty Ltd 27 Birubi Street, Cooparoo, Qld 4151. Tel: (07) 3394 3299

Besq 195 a microcrystalline wax. Dussek Campbell Pty. Ltd., Vic, 3026.

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Analysis, conservation and restoration of the metal threads used in Latin American colonial saints' robes

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Abstract

In this work we have analysed the silver and gold threads used for the decoration on the costumes of important religious sculpture from the colonial period and also one 19th C. statue of the Virgin Mary. Latin America had plenty of silver and gold mines not only during the colonial period but also in the 18th and 19th C. Silver and gold threads were frequently used in the embroidered decoration of the costumes adorning the most important, miraculous religious sculptures . The people of Latin America were very religious during that time.

This work presents the analyses and restoration on objects representative of three famous colonial sculpture schools in Latin America and the important school of Cataluña in Spain. The objects selected were:

Angel (school of Quito. Ecuador), *Saint Magdalena* and *Saint Frederick* (school of Cuzco, Peru) all from El Huique church,

a *Christ Child* and a *Textail (Pluvial)* (both from a school in Chile) from the Cathedral of Valdivia;and

a *Virgen del Carmen* from the patron of Santiago 19th C. Spanish school, Cataluña.

Keywords: Silver and gold thread, religious statuary, couching, over-use, rodent damage.

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1 Introduction

1.1 Some background concerning the history of mining in Chile:

Firstly, I would like to remind the reader that Chile is a country of great mining riches: particularly gold, silver and copper. During the Inca period, Chile was gave tribute to Perú in gold, which came from Marga-Marga. Extraction of gold from this source continued after the Spanish conquest. With the founding of La Serena in 1544, Concepción in 1550, La Imperial in 1551, Valdivia in 1552, and Osorno in 1554, the mineral pits and washeries of Andacollo, Quilacoya, Cautín, Madre de Dios and Ponzuelo were exploited respectively. The exploitation of the last four was terminated during the rebellion of the natives in 1959. The silver deposits, among others, Huantajaya, Copiapó and Huasco, in the North, Valdivia and El Chivato, in the central zone, have been exploited since the 13th century. These sites weresuperceded by the discovery of the silver in Azogue, in Punitaqui, from which the process of amalgamation was easier. The magnificent Casa de la Moneda, which is the current Palace of Government, was built in 1780 by Joaquín Toesca, and symbolizes the apogee of noble metal production along the 18th century.

The census of 1813 revealed the existence, between Copiapó and Talca, of 46 gold mines, 9 silver ones, 33 copper ones, one of lead, another one of quicksilver, 107 metal ore grinding mills, 27 silver-smelting blast furnaces for offerings of gold and silver and 52 casting machines. In the middle of the 19th century the mythical deposits of Chañarcillo and Arqueros would become the utmost as far as silver production was concerned. Their work throughout the colonial period has concentrated, not only in coin minting, but in objects for use in churches, for silverware for household use, and as well, for all kinds of objects (for example: fire-pans, tables, chairs, and even "small chamber pots"). It was a way, in the absence of banks, to keep control of personal wealth.

After the analysis, the restoration of the “gold and silver“ threads was completed as they were separated from the costumes. We have to say that after the analysis we found out that the the silver and gold threads were not so pure a silver and gold as the History of Art says. It is the second time that I have worked with colonial objects and discovered that the quality of the metal is not good. So it appears that the Spanish people in Latin America sent the best gold and silver home, and sold a misrepresentation to the Indian people.

Damage to the objects in the country church of El Huique was caused by the attacks of mice. In the Cathedral of Santiago and the Cathedral of Valdivia the damage is because the people use the sculptures in different religious ceremonies, so the sculptures reveal damage because of overuse.

1.2 Museum of the Cathedral of Valdivia

In 1997, I (Johanna Maria Theile) designed the Museum of the Cathedral of Valdivia, where I worked with colonial silver and gold articles in the museum’s custody. I also restored threads used in the embroidery of the chasubles and robes of the statues of the Saints and of Baby Jesus.

As already mentioned, religious art had great importance and significance in convincing the indigenes about the Catholic religion and in trying to maintain the faith of the Spaniards. This situation existed not only in Santiago but in the provinces as well. Missions began to be founded in different parts of the country. The mission in Valdivia was followed later by others carried out by the Jesuit and Franciscan clergy. Religious celebrations and ceremonies were very important, as for example, when the Marquez of Macera in repopulating the city of Valdivia in 1645 ordered “you shall have to take great care in that every Easter, days of Our Lady, apostles and patriarchs, all kinds of celebrations; and that people go to confession at least on Easter and Holy Week, and on the days of Our Lady the Virgin”. To carry out these celebrations, the clergy made great efforts in order to endow all the churches with rich holy amphorae, liturgical ornaments, paintings and sculptures. They even created carving workshops using the cypress and laurel in Valdivia. Tradition dictated that the saints and the clergy had to be dressed in robes embroidered with gold or silver threads. We see these objects today in the museum.

On February 1st, 1552 Pedro de Valdivia founded the city of Valdivia and the construction of the first principal church called Santa María la Blanca, whose patron was the Virgin of the Rosary, was commenced. Then, in 1559 the Main Church was made in Cal y Canto at the main square. Why was this cathedral so important? Because they were under threat from a number of sources. In 1599 the principal church was destroyed by the Huilliches and Mapuches (native indians of the area) who attacked Valdivia. Reconstructed in 1647, as a Family Vicariate dependent from the Bishop’s See of Concepción, it eventually became too small, and another church was built in 1712. But in 1748 a fire destroyed it, and another one was built. In 1870 the mother church was damaged by a water spout, and in 1907 it was damaged by an earth tremor. It was again destroyed in 1960 by an earthquake.

In 1988 the decision was taken to build a new cathedral. After a public bidding awarded to Mr. Jorge Swimburn Pereira, Jorge Swimburn Ríos and Alvaro Pedraza the new cathedral was built during ten years.

A modern church was inaugurated on October 9th, 1998. It was, at that time, decided to build a museum at the church. The help of Father Guarda was requested in order to carry out the museological design and I was asked to carry out the montage, conservation and restoring of the pieces. A museum with environmental control display windows, rail lighting, air conditioning, alarms, etc was thus created.

2. Techniques

2.1 Museum display cabinet

The museological notes were made by Father Guarda and a great deal of the work was carried out by us in Santiago at the Benedictine monastery. In the museological work, I designed a display window to be as perfect as possible, with a firm base in order to balance 42 school children (number of students in a normal class in Chile) without it tipping over. It was made of black non-polluting polyethylene (analysed with the Oddy Test), with a false floor in order to produce the correct microclimate, dry, because the environment of Valdivia is very humid. Black is the predominant color in the museum, to enhance the displayed objects since not all of them were of great quality. Part of the collection was donated in Santiago and another we received in Valdivia.

2.2 At the Cathedral of Valdivia

2.2.1 Analysis, Conservation and Restoration of the Pieces.

Among the donations to the museum were various silver and gold objects which were generally in good condition. Only one large silver object made to hold communion hosts had a loose base. It was fixed with grey Poxipol (Chilean Akimet) and the marks left by the paste were painted with Rembrandt acrylic paint. The biggest problems concerned laying the objects made of cloth, all of which were religious attire belonging to the Cathedral. They were certainly used previously in processions. In case of a mitre, it was necessary to reinforce the back part of the textile because it was made of silk, which had become embrittled. This work was carried out with the couching technique. All the loose gold and silver threads were tightened with silk threads using curved surgical needles. This mitre was used by the bishops of Valdivia and it dates back to the 18th century.

In the case of a pluvial (Figure 1) embroidered with birds and flowers, not only colour but also silver and gold threads were used. Damage due to use may be observed in it. Tightening the loose threads and reinforcing the pluvial on the back with a linen cloth was necessary to effect the restoration. Since it is very beautiful, a special display window was made where it is shown at a 45-degree angle to keep it from being damaged again.

Figure 1. The pluvial

Because this pluvial of the Virgen del Carmen (18th century) was one of the oldest objects of the museum which had decorations made with silver and gold, the threads used in this work were submitted to scientific analysis. Figures 2(a) and 2(b) show scanning electron microscope images of a thread at different magnifications. Figure 2(c) shows an x-ray fluorescence spectrum of the metal. The principal component is silver. The existence of trace gold, tin, and iron is evidence of the relatively crude extraction process which preceded the drawing of the thread.

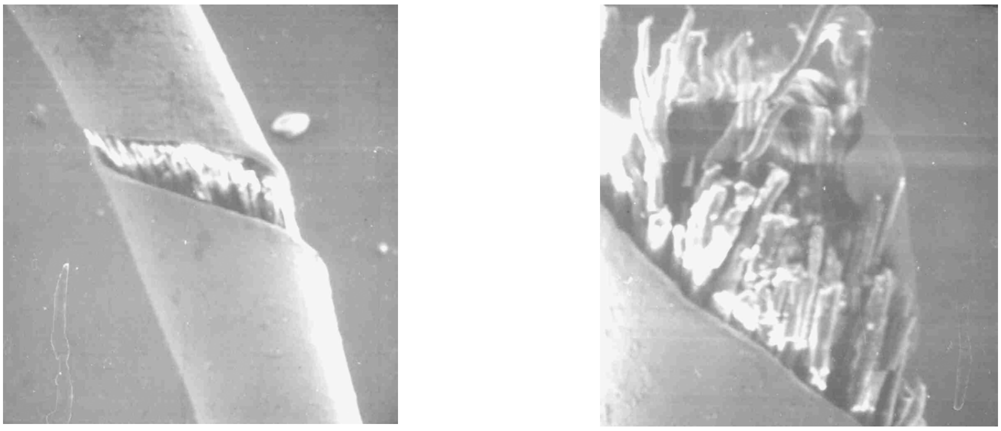

Figure 2. Thread image made up of a metal lamina (a) and interior threads (b).

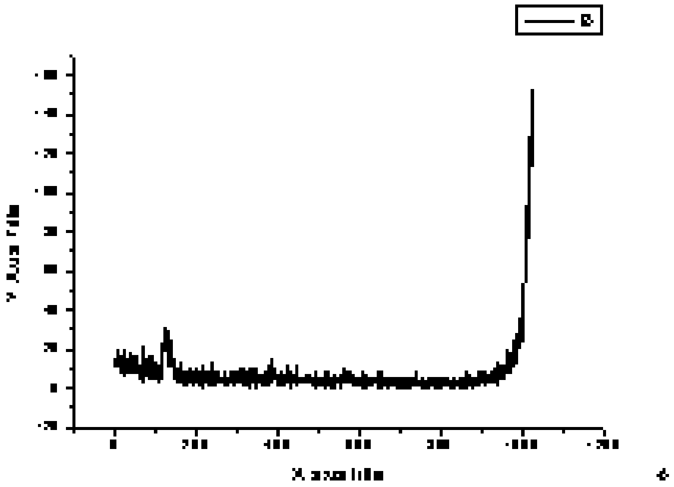

Figure 2(c). X-ray fluorescence spectrum of the composed thread. Detected elements in decreasing order of importance (KeV vs cps.): silver, tin, rhodium, palladium, copper, gold and iron.

In the case of a stole, the cloth was very worn and torn so it was very difficult to tighten the loose threads with the silk threads. As well, we had to restore its cloth since it was very brittle probably due to the weight of the silver threads.

The two processional crosses only had loose threads therefore their restoration was easy.

Figure 3. Baby Jesus and detail of his dress

The threads of the robe of Baby Jesus (Figure 3), which had come loose due to its presentation during Christmas on the manger of the altar, were also tightened. As can be seen from the figure, it was an important Baby Jesus, so the corresponding scientific analysis was also carried out on his robes.

The results of the analysis can be seen in Figures 4(a),(b), (c), and (d). Figures 4(a) and 4(b) show images of the thread and the surface of the thread. Figure 4(c) shows a region typical for deterioration of the protective varnish coating. Figure 4(d). shows an X-ray fluorescence spectrum of the lamina. Detected elements in decreasing order of importance are copper, zinc, iron, silver, antimony, tin and palladium. Again this shows that the thread was processed from relatively crudely refined ore.

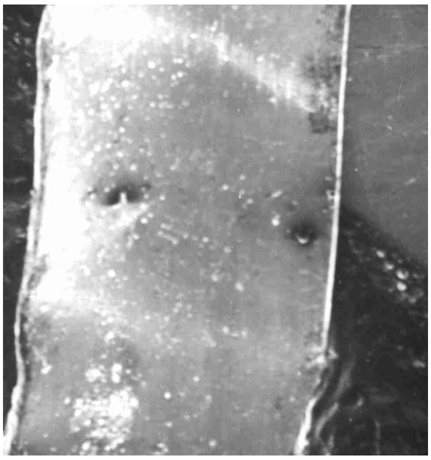

Figure 4a. Image of the laminar thread (SEM):

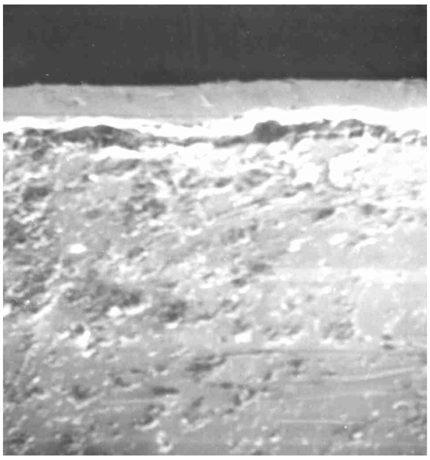

Figure 4b. Detail of the surface of the thread (SEM).

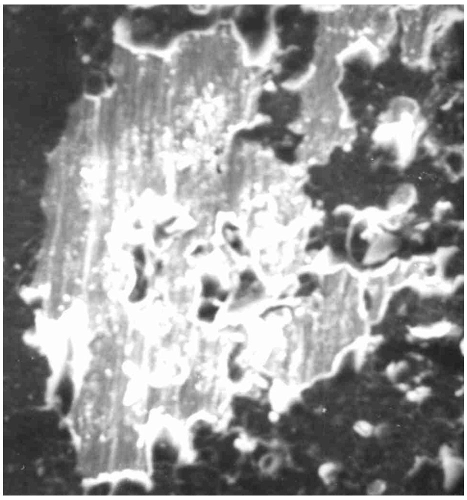

Figure 4c. Detail of the deteriorated surface varnish (SEM).

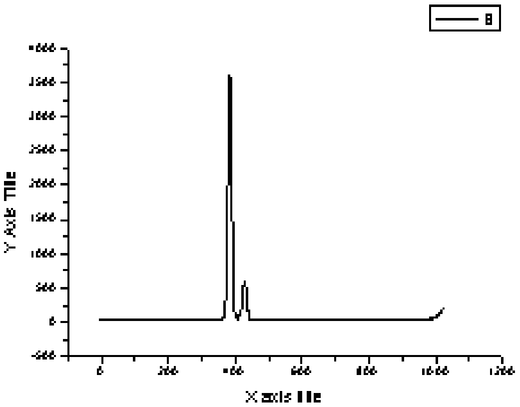

Figure 4d. X-ray fluorescence spectrum of the lamina. Detected elements in decreasing order of importance (KeV vs cps.): copper, zinc, iron, silver, antimony, tin and palladium.

The restoration work in the Museum of the Cathedral of Valdivia was carried out with students of the post-degree on Restoration They were the first students of the post-graduate degree in Restoration, during 1998.

2.2 At the Cathedral of Santiago

The city of Santiago de Chile was founded by Pedro de Valdivia on February 12th, 1541, at which time the cathedral was given a site. Construction work did not proceed until 1547. Called the Assumption of Our Lady in 1560, in 1560 it was substituted by a new factory, which in turn was destroyed by the earthquake of May 1647. This was destroyed and fell in the earthquake of 1679 and was replaced in June 1730.

The plans of the current cathedral were commended in 1753 to the Bavarian Jesuits Pedro Vogel and Juan Hagen. In 1780, when through the petition of Bishop Manuel de Alday y Aspee to King Charles III, the Roman architect Joaquin Toesca took over the work. He was followed by Juan Jose de Goycolea follows by Vicente Larraín, Eusebio Chelli, Fermin Vivaceta and Ignacio Cremonesi. The cathedral was finished in 1831 but it was only consecrated in 1906.

It keeps valuable paintings and works of gold and silversmiths, most of which were made by coadjutor Jesuit brothers who came from Bavaria. The collection went on to the cathedral after the expulsion of this religious order in 1767, most of these objects which are kept in the Museum of the Cathedral and others are displayed in the old sacristy.

2.3.1 Analysis, Conservation and Restoration:

The Cathedral of Santiago asked me to make a diagnosis of the state of its silver, gold and bronze collections in order to be able to restore them in a second phase. Gold did not pose any major problems, but the silver, which had been cleaned with great enthusiasm with a Chilean chemical product (Brasso^R), did. severely damaged the patina. All the religious objects of the chapel of the Holy Sacrament shone brightly. On the other hand, the main altar of the Cathedral made of platen (silver with copper) had some relief, and some parts of it were able to be saved. The person who did the work previously did not do the work meticulously, cleaning only that which was the easiest to clean: the surface. Some silver objects had been cleaned with a kind of crumbly, chalky lime, which left some scratches. Since the collection only had damage due to cleaning, and a patina cannot nor should not be forged, no restoration was carried out in the collection of the Cathedral. But the Bishop and his team were advised to use milder chemicals such as the product Tarnished Silver Cleaner on the colonial silver collection.

A theoretical-practical class was also given to the personnel of the museum in order to teach them how to use this chemical, since after applying the product; the object must be washed and thoroughly dried. Damage by chemical products used in cleaning could also be observed on the bronze objects. These were iron pieces dipped in bronze. The chemical ate away the bronze leaving the iron exposed.

Amongst these was a bronze fountain with was encrusted with green corrosion and stains produced by a very strong chemical, possibly an acid, that had burnt the surface of the fountain leaving brown rust circles. After analysing the fountain, it was discovered that the material was not bronze but brass. The origin of the circles could not be discovered. The green stains were eliminated mechanically with a scalpel (triangular). Efforts were made to remove the other stains with distillate water, but the auras remained visible. They were now clean but it was plain to see a missing piece of brass on the surface of each aura.

In the Cathedral a great collection of silver and gold embroidered textiles, chasubles, stoles, et cetera, exists. Because the Cathedral authorities are concerned for the state of their collection, the Museum asked me to restore a very beautiful processional cross which has a red background embroidered with silver and gold religious themes. The silver threads had become loose and the image had been damaged since this cross had been frequently used in processions. The external gold fringes, which were added to the object 10 years ago to make it look more beautiful, were in good condition. In the restoration, the silver threads were attached to the cloth with silk threads and surgical needles. No new threads were used. In some parts, the original silver thread was missing; certainly someone must have taken it as a souvenir. The Museum wanted the eye of the Saint to be painted again. This I did not do since there was no information on it in order to know how it was, who our saint was looking at.

In the cathedral itself there is a sculpture of the Virgen del Carmen. It is a life size wooden structure with a porcelain face and dressed (Figure 5a). The Virgen del Carmen is the Patroness of Chile. The robe is full of silver and gold thread embroidery. Since she is deeply venerated and frequently touched by the faithful who go to ask for her help, many ornaments had become loose. All of the silver and gold threads and the ornaments were put back in place on the cloak using silk threads and curved surgical needles. Once the work was finished, it was again put on public display since in the Cathedral of Santiago the Virgen del Carmen cannot be allowed to be absent from her station.

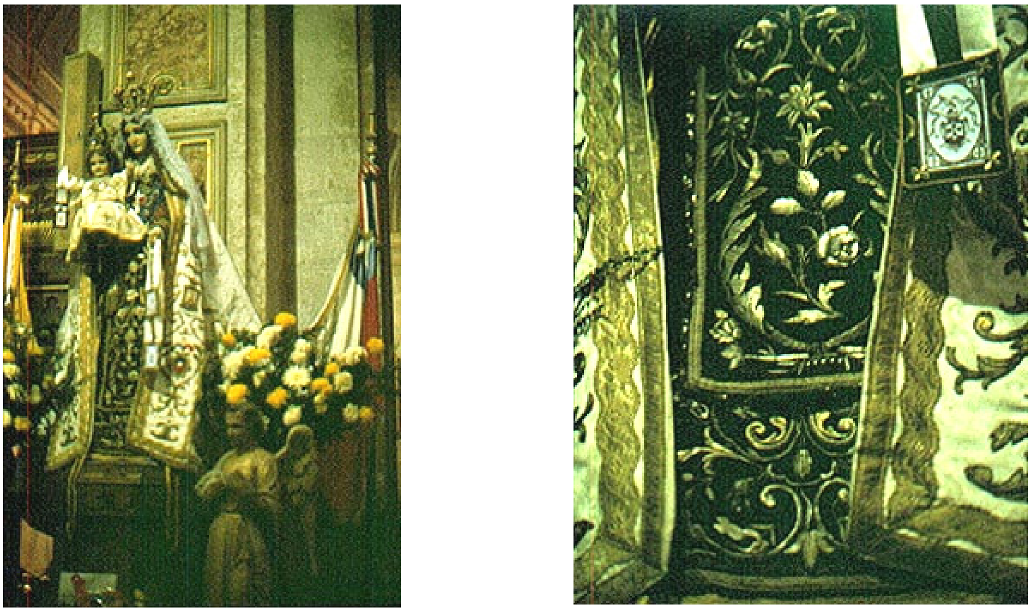

Figure 5(a). Photograph of the Virgen del Carmen and detail of her dress

The Virgen del Carmen comes from the school of Cataluña. The cathedral was asked for authorization in order to carry out a study on the silver and gold threads used in the embroidery of her cloak so as to also have in our investigation an object from our Mother Land. Thus we would be able to observe the extent to which there was an influence of the Spanish techniques on the manufacturing of threads in Latin America.

The results of the analysis (Figure 5 b) showed the principal components of the thread to be copper, silver, and gold.

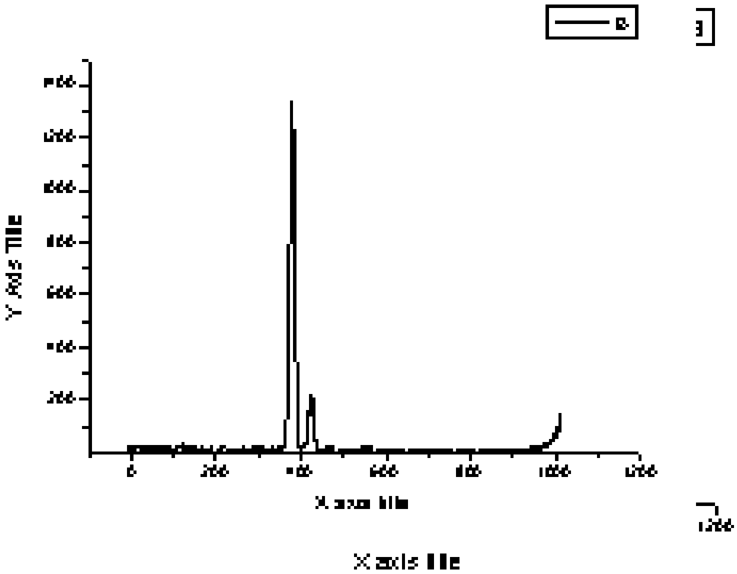

Figure 5(b) X-ray fluorescence spectrum of the composed thread. Detected elements in decreasing order of importance (KeV vs cps.): copper, silver, gold, tin, zinc, antimony and iron

2.4 Saint José del Carmen in El Huique

Continuing on the topic of the silver and gold threads used in the robes of religious saints I here describe my work in the Hacienda of El Huique in December of 2002, which is currently an important National Monument, now turned into a museum, the "museum of Saint José del Carmen of El Huique"

The property has its origins in the great Hacienda Larmagüe, which extended over 30,000 hectares, lying between the Cachapoal and Tinguiririca rivers (central zone of Chile, near the city of Santa Cruz).

The farm was the property of Ms. Paula Mercedes de Lecaros y Lecaros, married to Mr. Pedro Gregorio de Echeñique. The property was in the hands of this same family for six generations. Larmagúe was divided for the first time in the 18th century among the children of Mr. Pedro Lecaros.

El Huique for Mr. Miguel de Echeñique and El Almahue for his brother Antonio, the main house that is currently the museum rebuilt at the beginning of the 19th century. Later on, Mr. Miguel Echeñique divided his part among his three sons. The youngest of them receives the Hacienda calling it Saint José del Carmen of El Huique and began to build the house immediately in 1829 having 20,000 square meters including patios and dependencies.

El Huique is important for our Cultural Patrimony not only because it represents a typical Hacienda of the 19th century but also because it was the property of one of the presidents of Chile, President Federico Errázuriz Echaurren who was in office as president of Chile between 1871-1876, spending the hot summer in El Huique with his family.

El Huique also has a beautiful church which has a façade with a 23 meter tower, crowned by a copper dome. The person in charge of the building of the church was Mr. Juan José Echeñique Bascuñan approximately in 1857. It has a Baroque style, wooden carved altars with applications of leaves of gold and marbled, balusters with Murano crystal. This is a most beautiful country church, perhaps the best in Chile. It has sculptures of great artistic value inside, especially the Quiteño angels, the Nazarene colonial Christ, Saint Frederick and Saint Magdalene.

2.3.1 Analysis, conservation and restoration of some of the pieces of the Museum

I created in El Huique a conservation laboratory where we restored a Nazarene Christ with damage caused by people who pulled on the threads, a Quiteño angel who had been attacked by termites (Figure 6a), Saint Magdalene (Figure 7a) and Saint Frederick (Figure 8a). They had damage caused by mice on the lower part of their robes. This is a common problem for *in situ* museums, which are surrounded by farmlands.

Figure 6 . Colonial Angel of the School of Quito.

The images and X-ray fluorescence spectrum of the threads used in the decoration of the dress of the Colonial Angel is shown in Figures 6(a, b, c and d).

Figure 6a. Image of the laminar thread (SEM):

Figure 6b. Detail of the surface of the thread (SEM).

Figure 6 c. Detail of the deteriorated surface varnish (SEM).

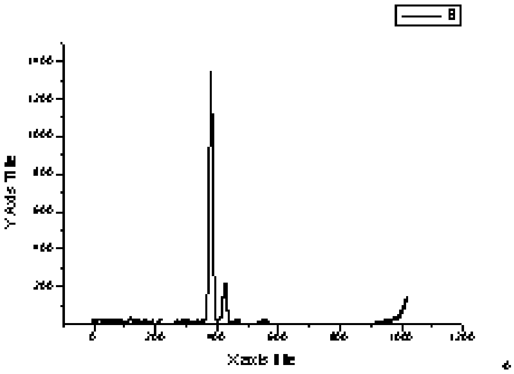

Figure 6d. X-ray fluorescence spectrum of the lamina. Detected elements in decreasing order of importance (KeV vs cps.): copper, zinc, rhodium, silver, antimony, tin, gold. palladium and iron.

The angel has damage to its structure due to termites, and, as well the lower part of its robe has also been damaged by mice. To eliminate the termites, each hole in the angel was disinfected with Xylamon, and later each hole was sealed with virgin wax, so that a new attack could easily be identified in that way.

In order to strengthen the robe, the damaged parts were reinforced with natural linen, attaching it to the original cloth, which was the same colour. It was done with silk thread using surgical needles; the loose threads of the robe were also tightened.

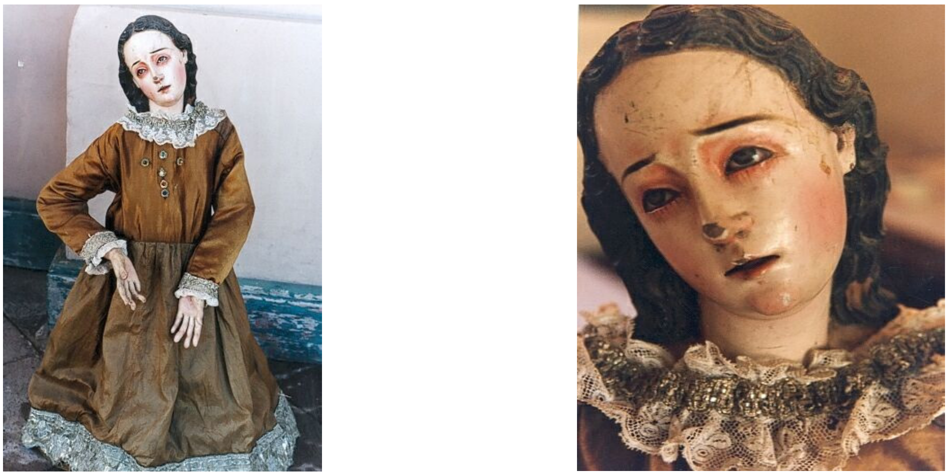

Figure 7a. Saint Magdalene, colonial, School of Cuzco

The images and X-ray fluorescence spectrum of the threads used in the decoration of the dress of the Saint Magdalene are shown in Figures 7 (b and c).

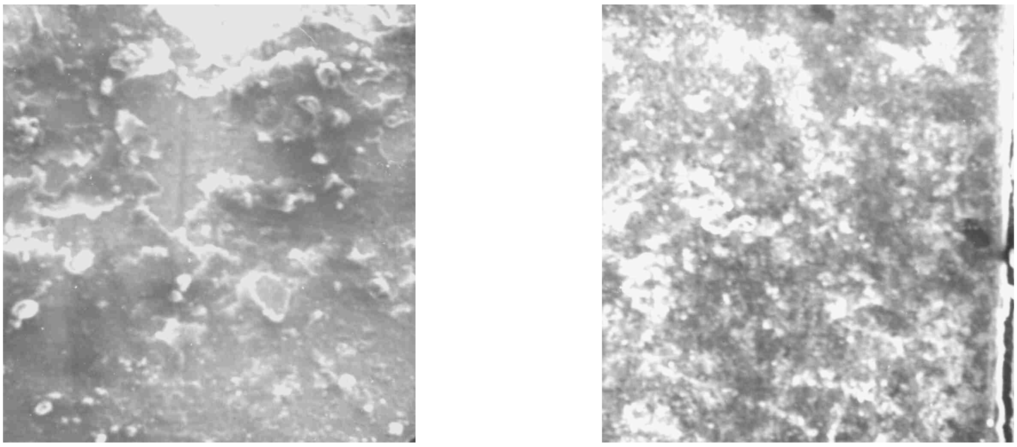

Figure 7b. Image of the metallic lamina and its deteriorated superficial varnish (SEM).

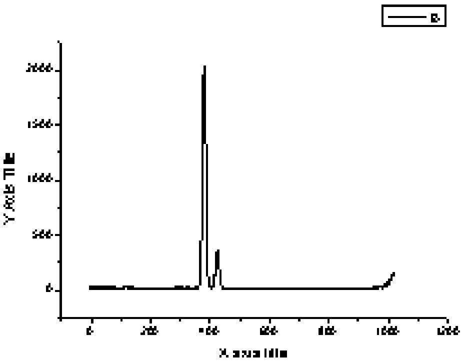

Figure 7c X-Ray fluorescence spectrum of the composed thread. Detected elements in decreasing order of importance (KeV vs cps): copper, silver, zinc, antimony, tin and iron.

In the inside of the sculpture, Saint Frederick, School of Cuzco Saints, did not have a body but only a staff, which supported the head and the arms. Again the couching technique was used in the restoration of his robe in order to put the threads back to their place.

Figure 8a. Saint Frederick, colonial, School of Cuzco

The images and X-ray fluorescence spectrum of the threads used in the decoration of the dress of the Saint Frederick is shown in Figures 8 (b and c).

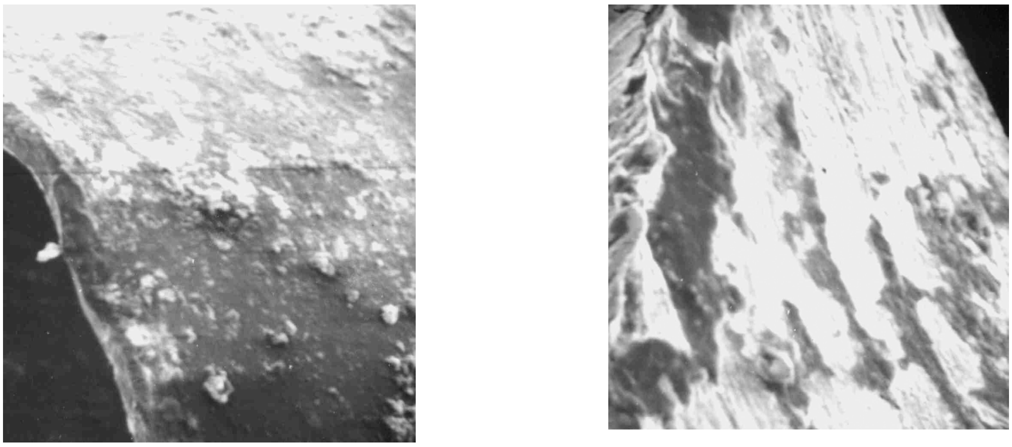

Figure 8b. Image of the metallic lamina and its deteriorated superficial varnish (SEM).

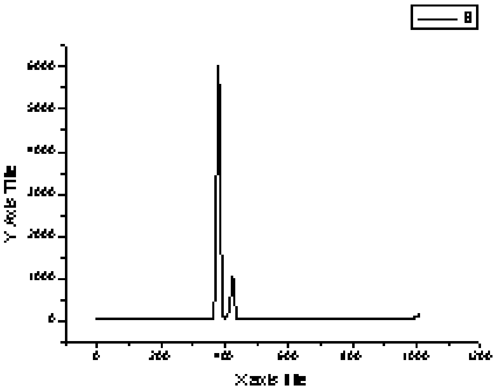

Figure 8c. X-ray fluorescence spectrum of the composed thread. Detected elements in decreasing order of importance (KeV vs cps): copper, zinc, silver, tin, antimony and iron.

This saint had the lower part of his robe very eaten away by mice, so we had to make a graft from a cloth similar to the original, in order to reconstitute the dress. The couching technique was used for all the work of restoration.

3. Summary of results

Table 1 is a summary of the analyses carried out giving the relative elementary composition of the constituents in (wt %)

It can be readily seen that the "gold and silver" threads are not of great purity, indicating that the techniques for the purification of the metals were quite primitive. Previously, a study in colonial silverwork (insert reference) was carried out in which the objects from Chilean religious art analysed were also metals of much lower category than those quoted in the literature.

Table 1. Relative elementary composition (wt %) obtained by X-ray fluorescence spectrometry.

No.	Sample	Fe	Cu	Zn	Au	Ag	Sn	Sb	Rh	Pd
1	Pluvial Cathedral of Valdivia	0,02	0,05	0,00	0,03	98,34	0,48	0,00	0,28	0,80
2	Baby Jesus	0,20	97,81	1,49	0,00	0,19	0,10	0,10	0,00	0,11
3	Virgen del Carmen	0,24	95,75	0,29	0,53	2,51	0,43	0,26	0,00	0,00
4	Saint Magdalene	0,12	96,69	0,25	0,00	2,59	0,14	0,21	0,00	0,00
5	Quiteño Angel	0,21	93,67	4,06	0,00	0,58	0,33	0,49	0,44	0,24
6	Saint Frederick	0,06	98,17	1,23	0,00	0,28	0,16	0,10	0,00	0,00

For me it was a pleasure to be able to work in the collections presented in this paper for each piece was a beauty, and besides, they were a challenge to restore.

As it can be appreciated, in this project the conservation of pieces, which are important for National Patrimony, has been achieved and new information on the composition of Chilean colonial silverwork has been obtained.

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Cremated: Analysis of the metalwork from an Iron Age grave

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Abstract

The grave finds from an Iron Age cremation in southern England include a group of iron implements and a copper pin. The condition of the metalwork is quite exceptional. Surface deposits on the iron implements reveal traces of haematite, whereas the copper pin is covered in a thick layer of tenorite. These deposits are high temperature oxidation products deriving from the cremation pyre rather than from corrosion processes.

Résumé

Les trouvailles d'une tombe à incinération de l'age de fer dans le sud de l'Angleterre inclurent un groupe des instruments en fer et une épingle en cuivre. La condition de préservation de ces objets de métal est bien exceptionnelle. Des couches sur la surface des instruments de fer contiennent de hématite tandis que l'épingle en cuivre est couvrit d'une forte couche de ténorite. Ces couches sont les résultats d'oxydation à hautes températures provenant plutôt du bûcher de crémation que des procès de corrosion.

Keywords: haematite, tenorite, XRD, XRF, SEM

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1. Introduction

A group of implements, probably part of a craftsman's tool kit, was recovered with a cremation burial at the prehistoric site at White Horse Stone, Kent, in southern England (Figureure 1). The cremation is radiocarbon dated to 490 – 160 cal BC. The shallow cremation pit was excavated in 1998 by Oxford Archaeology in advance of extensive development for the channel tunnel rail link, for CTRL (UK) Limited.

The group of implements comprises two iron knives, four iron awls and a whetstone, plus a small loop-headed copper pin. The awls may well have been used for working skin products, conceivably untanned hide rather than leather owing to their large size, or coarse textile. The small knife would be very suitable for cutting skin, leather or fibres. On balance however, it seems possible that the implements once formed part of a tool kit of a skin or leather worker.

The condition of the metalwork is quite exceptional. The iron implements are only superficially corroded, with fine surface detail preserved and clearly visible under the chalky soil deposits. For example, the larger knife has a clear bevel on both sides of the cutting edge. The tips of the awls remain sharp and their tangs are pristine. However, there is no evidence of any associated mineralised organic materials such as handles. Instead, there are small areas of bright red deposits near to or on the tangs of four of the six iron implements. Another distinctive feature of the awls and larger knife is the dense and lustrous, dark grey to black appearance of the metal surface under the soil (or under the red deposits).

The non-ferrous metal pin is covered with a thick layer of porous black powder with occasional green areas visible. As a consequence of its appearance, the pin was initially thought to be made of a silver alloy.

It is generally assumed that bright red deposits on archaeological ironwork are often haematite resulting from burning in oxidising atmospheres. This red colour is invariably present on freshly forged iron together with a very smooth and compact black oxide layer. One of the first people to comment on the presence of haematite on

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Figure 1. Metal artifacts from the cremation pit

burnt archaeological iron was Leo Biek, who noted in particular that haematite was a component of fire-scale on freshly forged iron, and it could also be formed as a consequence of conflagrations of buildings and other structures (Biek 1963, 133-4; Blackwell and Biek 1985). Other citations for cremated ironwork include King Harry Lane cemetery, Hertfordshire, where three iron nails were found to be in 'pristine condition having been burnt with the 'calcined bones' (Stead and Rigby 1989, 111). At Westhampnett Bypass, West Sussex, the fired metalwork was noted for its fragmentary condition, discolouration and distortion or 'molten' appearance (Northover and Montague 1997). On the continent, the well preserved iron surgical implements from a Middle Iron Age cremation in Bavaria are described as having a 'fine fire-patina' (de Navarro 1955, 232).

Despite this general acceptance, analysis of the deposits on archaeological artifacts does not seem to have been attempted. This group of iron implements provided the opportunity to characterise the surface layers and to determine how they relate to the cremation.

2. Methods of analysis

The implements were initially x-rayed and also examined under a binocular microscope at low magnification for features of relevance to their technical descriptions. This included close examination for evidence of mineral preserved organic materials such as handles and containers.

The pin was analysed by energy-dispersive x-ray fluorescence (XRF) in an Eagle II x-ray fluorescence spectrometer with lithium-drifted silicon detector. A sample of the black deposit from the head of this pin was removed for x-ray diffraction (XRD) analysis, and the pin was again analysed by XRF to verify that the composition did not alter substantially below these layers. Surface samples from three awls and the larger knife were also analysed by XRD.

Samples in the order of 1 mg were ground in an agate mortar and mounted on a flat single-crystal silicon sample holder, designed to reduce background scatter. X-ray diffraction data were collected on a Philips PW1840 diffractometer using cobalt K_α radiation (wavelength 0.179026 nm) incorporating a solid-state silicon detector. A search-match computer programme (Philips, based on JCPDS files) was used to identify unknown components in the diffraction patterns by comparison with standards in the powder diffraction file. Jeweller's rouge powder (haematite) was also employed as a standard.

The larger knife was also sampled for metallographic examination (see Figure 1), which will be reported on elsewhere, although the opportunity was taken to examine the oxidation layers by scanning electron microscopy with energy-dispersive x-ray analysis (SEM-EDS) in a Leo 4401 Stereoscan electron microscope.

3. Results

XRF analysis of the pin showed that it was made of relatively pure copper with a trace of tin (Figure 2). The crystalline components determined by XRD are shown in Table 1. The black deposit from the surface of the pin was tenorite (CuO). Samples of the red deposits from the iron implements comprised haematite (Fe_2O_3), sometimes with calcite ($CaCO_3$) plus trace amounts of soil components, such as quartz. Samples of the grey-black layers on the iron comprised mainly magnetite (Fe_3O_4), with goethite (FeOOH) and lesser amounts of haematite and calcite.

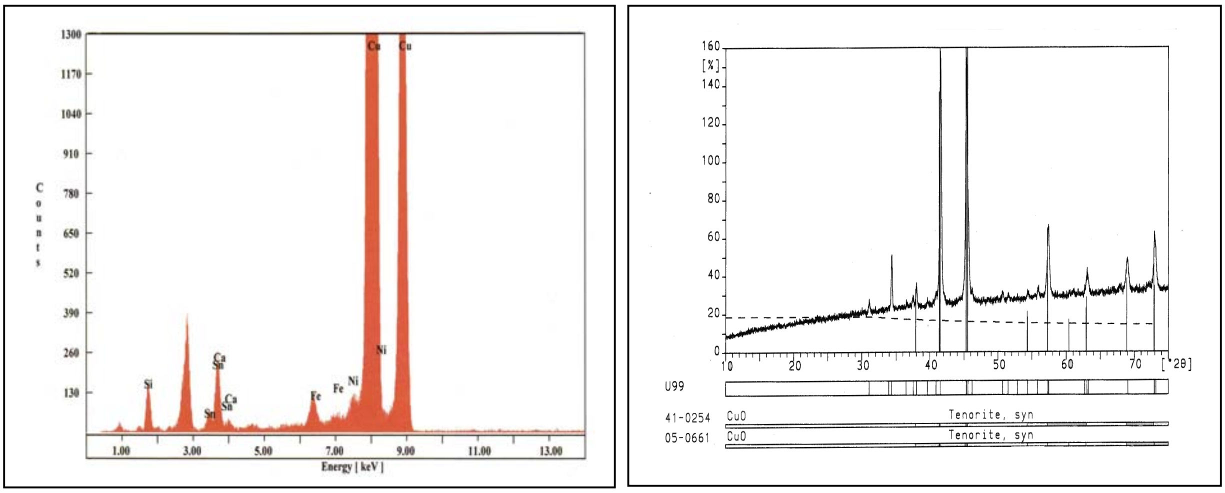

Figure 2. Non-ferrous metal pin 112. Left: XRF spectrum shows copper to be dominant. Right: XRD spectrum of the surface black layer shows mainly tenorite

Table 1. Results of XRD analysis

Artifact	**Sample**	**Crystalline components**
Knife 106	Red deposit from the tang	**calcite** haematite
Awl 107	Corrosion blister from stem	**magnetite** goethite (haematite)
Awl 107	Grey-black product from stem	**magnetite** goethite (calcite haematite)
Awl 108	Red deposit from the tang	**calcite** haematite
Awl 108	Grey-black product from stem	**magnetite** **goethite** (haematite calcite)
Awl 110	Red deposit from the tang tip	(haematite)
Pin 112	Black powder from the head	**tenorite**

Major constituents shown bold, minor shown normal and trace levels are bracketed

Analysis of the oxidation layers by SEM-EDS did not show any significant difference in oxygen concentrations between the metal and the outer surface. However, the thin oxidation layer of c. 100 µm thickness did reveal a distinct compact and well-formed outer layer of c. 15 µm thickness (Figure 3). There was also a compact middle layer, which in places had a columnar appearance; whereas the innermost oxidation layer appeared more ragged, presumably where corrosion has occurred.

4. Discussion

When iron is heated in air it forms multi-layered oxide scales comprising wüstite (FeO), magnetite and haematite, the precise composition of which is temperature dependent (Birks and Meier 1983). Wüstite is the most iron-rich oxide, forming adjacent to the metal, whereas haematite is the most oxygen-rich, forming next to the atmosphere. Heating below 570°C, a two-layered scale develops consisting of magnetite next to the metal and haematite on the surface. Above 570°C, wüstite forms below the other two iron oxides, next to the metal, giving the sequence: metal, FeO, Fe_3O_4, Fe_2O_3 — the ratio of which are roughly 95:4:1 at 1000°C (Birks and Meier 1983, 75). Through the migration of electrons outwards, the scales increase in thickness particularly at elevated temperatures when the wüstite will form the thickest layer. Nevertheless, this wüstite layer is unstable and will break down to iron and magnetite below 570°C under certain conditions (Kofstad 1988, 9). However, if wüstite is quenched or rapidly cooled, it can be retained without transformation (Scully 1990, 39; Massalski et al. 1990, 1742). Factors such as temperature and partial pressure of oxygen will affect the growth rate and composition of the various oxides, as well as the precise phases to be formed. The latter will affect the defect structure of the crystals and their electrical conductivity and, presumably, stability over time and stability in the ground.

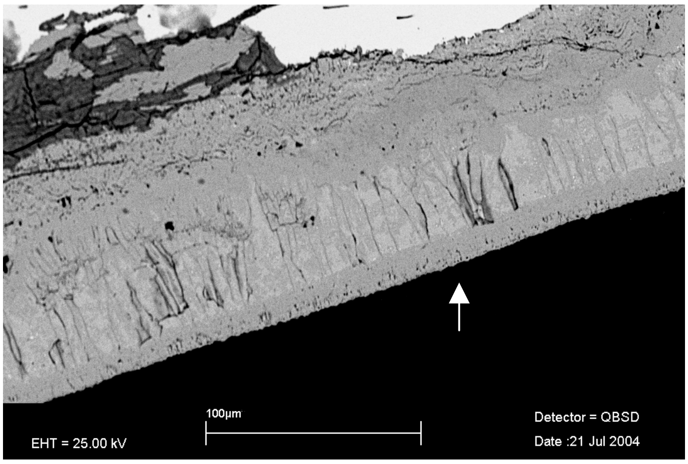

Figure 3. Backscattered electron image of section through the iron knife 106, showing metal at the top (light) with slag (dark grey), oxidised layers running diagonally across the centre (pale grey, c. 100 µm thick), and mountant at the base (black). Note the well-formed outer oxidation layers, in particular at the surface (arrowed).

The nature of the oxide phases – dependent on the factors described above – may explain why burnt iron artifacts often retain the distinctive grey/black surfaces which are usually resistant to corrosion. These layers are very similar to those on flake hammerscale, the by-product from the forging of iron and often found on archaeological excavations at the sites of smithing hearths (McDonnell 1986, 48). Sometimes archaeological burnt iron artifacts are found in hollow condition – a phenomenon reminiscent of spherical hammerscale with its dark and lustrous skin of variable compositions comprising wüstite, magnetite, and fayalite ($2FeO.SiO_2$) and other glassy components due to the presence of slag from the smelting process (Unglik 1991). However, the explanation for the hollowness of the examples may be different. In the artifacts it seems likely that if the protective layer of well-formed magnetite becomes damaged, perhaps as a result of contraction during cooling, a corrosion cell might develop, leading potentially to voiding due to corrosion. A contraction effect may be visible at the centre of the oxidation layer in Figure 3.

The presence of haematite on the archaeological ironwork from White Horse Stone suggests that the implements were fired in the cremation. The lack of a handle on any of the implements supports this, and the handles themselves may have provided additional fuel for the cremation given that the haematite is present on or near to the tangs of the implements. The other iron oxides present, magnetite and goethite, are probably a mixture of high temperature oxidation products and corrosion products. Certainly the appearance of the ironwork, with its dark and lustrous surface that has protected the surface detail, suggests that the firing process has been critical to its exceptional condition.

The thick black surface layer of the copper pin from the grave group comprises tenorite suggesting that this artifact was also likely to have been placed in the cremation. When copper is heated in oxidising atmospheres it will invariably yield the black cupric oxide, tenorite ($Cu0$), familiar to everyone who has annealed or soldered any modern copper alloy. Beneath this, closer to the metal, there will form the red cuprous oxide, cuprite (Cu_20) sometimes visible as a thin pink layer on initial heating (Untracht 1982, 416) and forming at lower partial pressure of oxygen.

In summary, the metalwork from this cremation was shown to have oxide layers which are characteristic of heating to high temperatures in normal or oxidizing atmospheres. These finds were presumably placed on the cremation pyre. The iron in particular has been preserved in an exceptional condition due to the protective nature of the oxide layers.

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