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METALS CONSERVATION AT THE WESTERN AUSTRALIAN MUSEUM

BEING A DISSERTATION SUBMITTED FOR

THE DEGREE OF MASTER OF THE CANBERRA

COLLEGE OF ADVANCED EDUCATION

BY

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Preface

It would be impossible and I believe unprofitable to detail all the activities I engaged in at the WA Conservation Laboratories. The usual housekeeping tasks are not recorded nor is each and every calibration curve preceding a daily analysis. Time spent in publicity activities such as being the subject for a "Simon and Townsend Wonderworld" segment or a picture for a WA newspaper, taking part in consultations with members of the public or other sections, days spent weighing and measuring numerous bronze bars and pins - all these occurred but are not discussed. They were not central to my purpose which was to record the unique and different aspects of the activities of the host institution as I experienced them and to assist my understanding of the basic processes of corrosion and its treatment. Some of the most important benefits of an internship cannot be recorded directly. They are the sum of conversations with professional conservators on topics unrelated to the main theme of studies undertaken; observed attitudes and stratagems used for solving problems that arose. This style depends greatly on the personalities present at the time and I am delighted to have had such stimulating and informed company.

The staff at the WA Museum conservation section have between them an impressive range of talents and it is regretted that there was not enough time to spend several months working with each of them.

However, I consider myself fortunate to have had Dr. MacLeod as a supervisor and thank him for his unfailing patience and guidance.

Sincere thanks are also due to Dr. Neil North who kindly accepted me into his domain and obtained the monies to finance an internship.

Jennifer Edwards

July, 1982

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4. Chloride Levels and Release Rates During the Washing of Copper Nails from the "Rapid"

SUMMARY OF WORK AT THE WESTERN AUSTRALIAN MUSEUM DURING THE PERIOD JANUARY - JUNE 1982

The following pages are a record of work done during my internship at the W.A. Museum's Conservation Laboratories.

The record following is not in chronological order as all tasks overlapped, but has been grouped into:

(1) records of treatments and investigations in which I played a part, and

(2) experimental work on chloride release rates,

(3) one other section gives a description of the conservation facilities at the museum as they relate to its function.

Metal conservation involves treatments which may take years to complete. Thus not all treatments discussed in these papers could be either completed or begun by myself. No complex conservation treatments were underway during my stay and the examples I have detailed are intended as a first hand record of standard procedures for the most common non ferrous metals conserved at the W.A. Museum and the rationale for such treatments.

Work sheets which are collated data for experimental work, together with graphical representations of this data is annexed to the report.

Photographs have been copied on a colour copier and I am advised they are to be considered archival quality. The negatives either black and white or colour slides have been retained and stored by the W.A. Museum and therefore their W.A. file numbers are quoted in annex (5) and, for SEM illustrations in the text as well.

BARBER'S BOWL (REG NO. GT3053)

History and Previous Conservation

This object had been recovered in 1981 from the wreck of the Vergulde Draeck (1656). The dimensions of the bowl are shown in Figure 1a, 1b and 1c.

The bowl had been treated; concretions removed and washed for 3212 hrs in 1% w/v sesquicarbonate with the release of 150 mg of chloride. It had subsequently been soaked in alcoholic benzotriazole 3% w/v for 29 days.

Analysis - none, as the object was considered "too valuable" for any destructive analysis. From the colour it is a "yellow brass".

Condition

The bowl was a pale brassy colour with some areas of dark patina which are often seen on zinc containing copper alloys recovered from the sea. The rim and bowl had many areas of irregular corrosion attack indicating an anaerobic marine environment containing sulphate reducing bacteria. The bowl was very thin and fragile and its centre was perforated in several places. The corrosion pattern in such cases varies in profile probably a result of localised variations in the microbiological population. The bowl had been "protected" from normal sea water by an enveloping iron concretion which was removed on the site. The major copper corrosion product was Cu_2S (chalcocite) while there were also large amounts of magnetite (Fe_3O_4) and aragonite. ($CaCO_3$)

Treatment

After consultation with the marine archaeologist who was the bowl's designated curator it was decided to "Incralac" this object. Wax treatments had proved unsatisfactory in the maritime museum because of the continual ingress of salt containing dusts into the galleries from walls and the outside environment.

It was therefore given 2 coats of "Incralac"* in 60% v/v thinner 341* allowing 24 hrs between coats. The operation was performed in a fume hood and application was done using a combination of dip and brush techniques.

When the coats had dried and cured the bowl was packed with the bowl opening upwards in a ventilated cardboard box into which a ring support padded with acid free tissue had been firmly attached. This allowed the weight of the bowl to be taken up by the relatively sound rim.

* Wattyl brand

The bowl itself was loosely wrapped in acid free tissue and the spaces between the object and the walls were also padded out with folds of tissue. After the box was closed a label sealed in plastic was attached to the outside stating the object's number and its descriptive title above a simple outline drawing of the bowl.

The bowl was stored with other finished articles in a metal cabinet and was selected at the ANCOD divisions, 1982 to form part of the national collection held in Canberra by the National Heritage Commission Council.

Recommendations for Storage and Display

This article is vulnerable to mechanical damage and high humidity.

It should not be rested on its rounded base and both in storage and display supported beneath the rim.

Relative humidity should not be allowed to exceed 60%.

Handle wearing gloves

At any sign of "bronze disease" place in a suitable sealed container together with at least 300g of self indicating silica gel and seek conservation advice.

<u>Attachments</u>: (1) Photographs - Before and after conservation - illustrations 1 and 2 pg10

(2) Sketches of bowl and its dimensions: Fig 1a, 1b and 1c pg 7,8,9

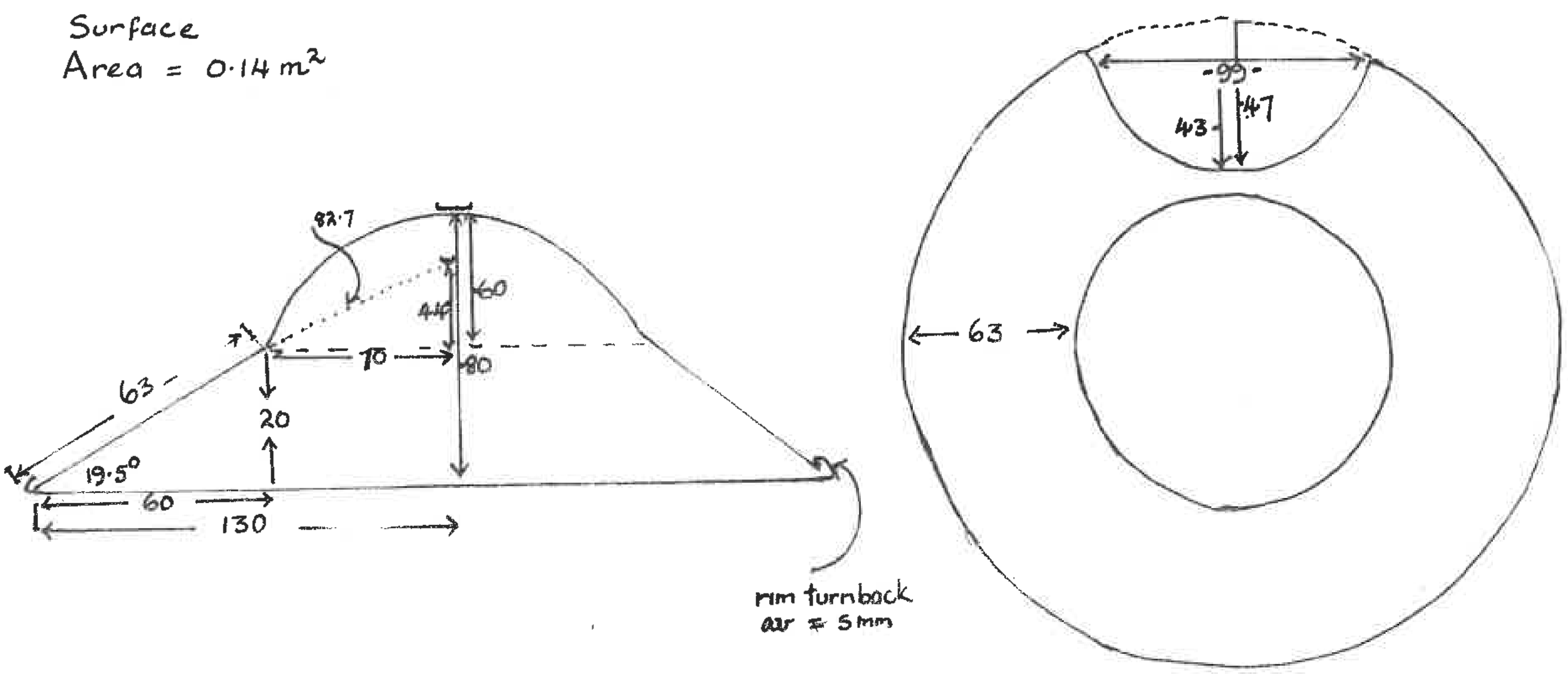


Fig 1a <u>Dimensions of the Barber's Bowl (Reg No GT 3053) recovered from Vergulde Draeck, 1981</u>

<u>Dimensions shown are in mm.</u>

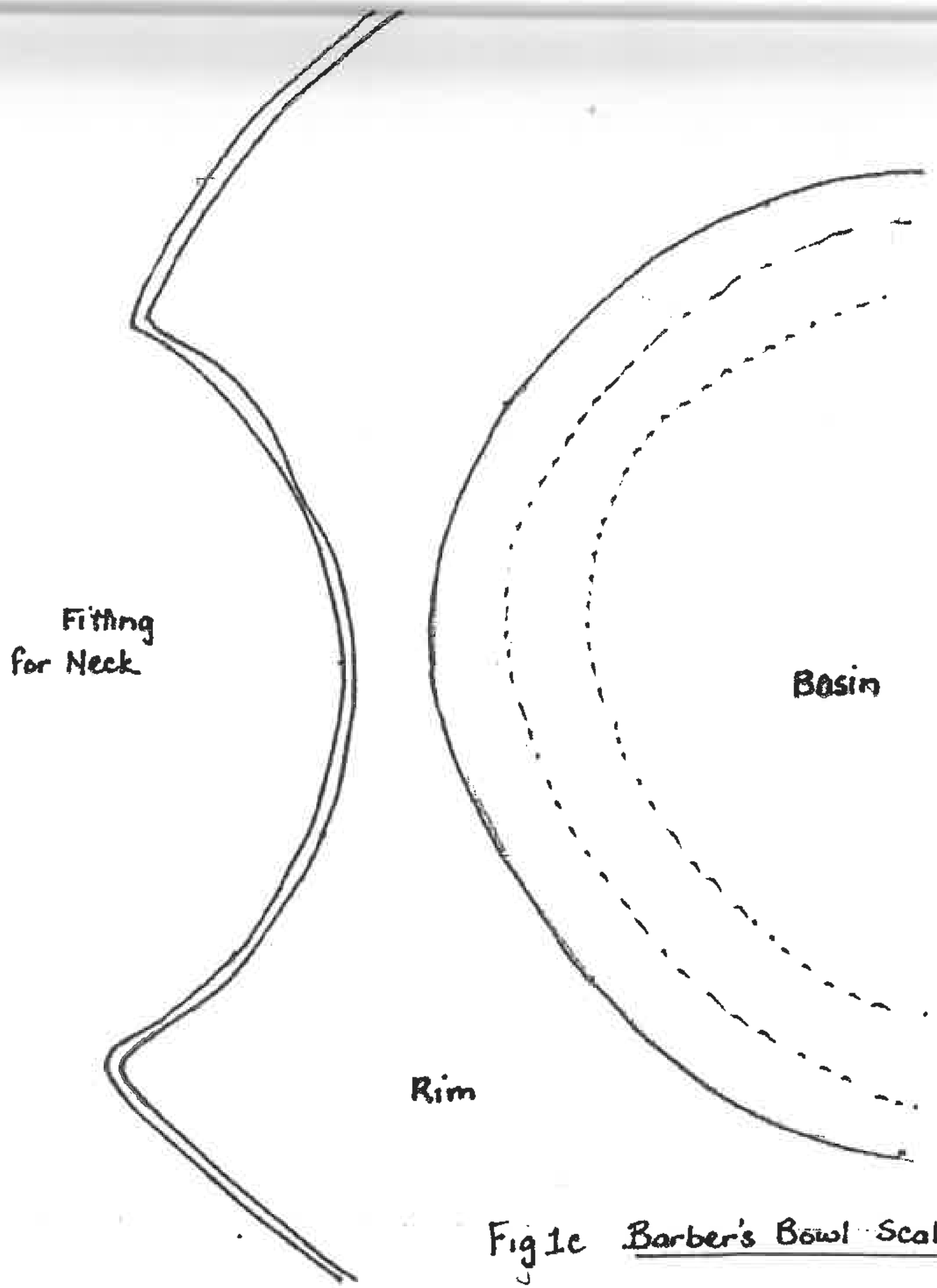


Fig 1c Barber's Bowl Scale Drawing - Neck Fitting

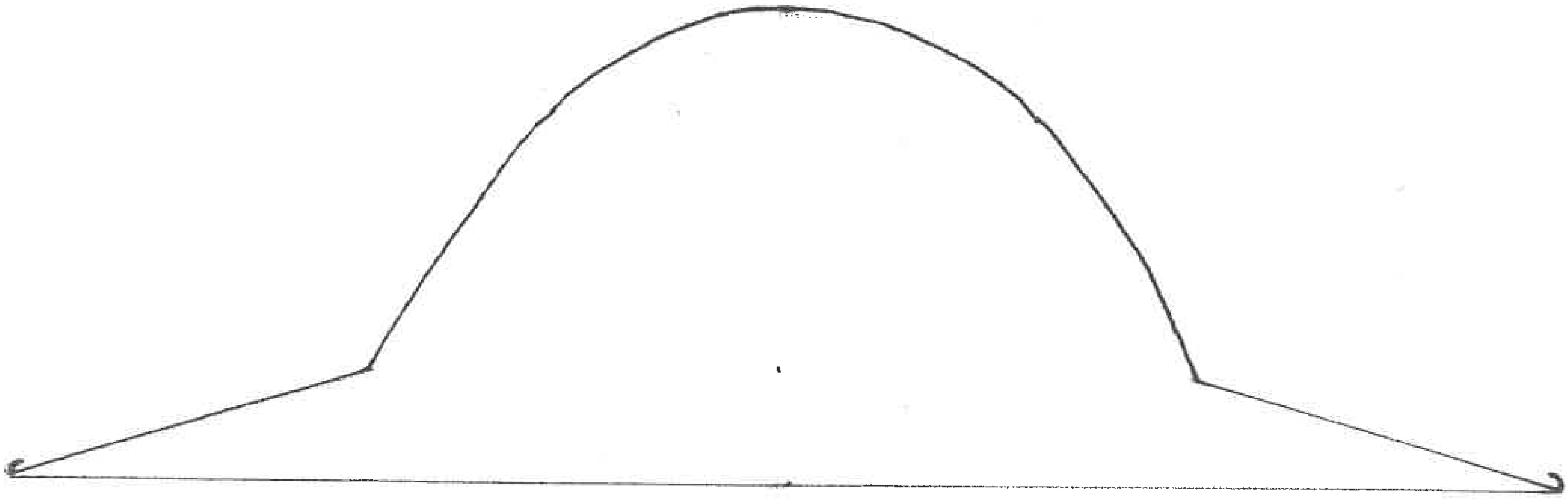
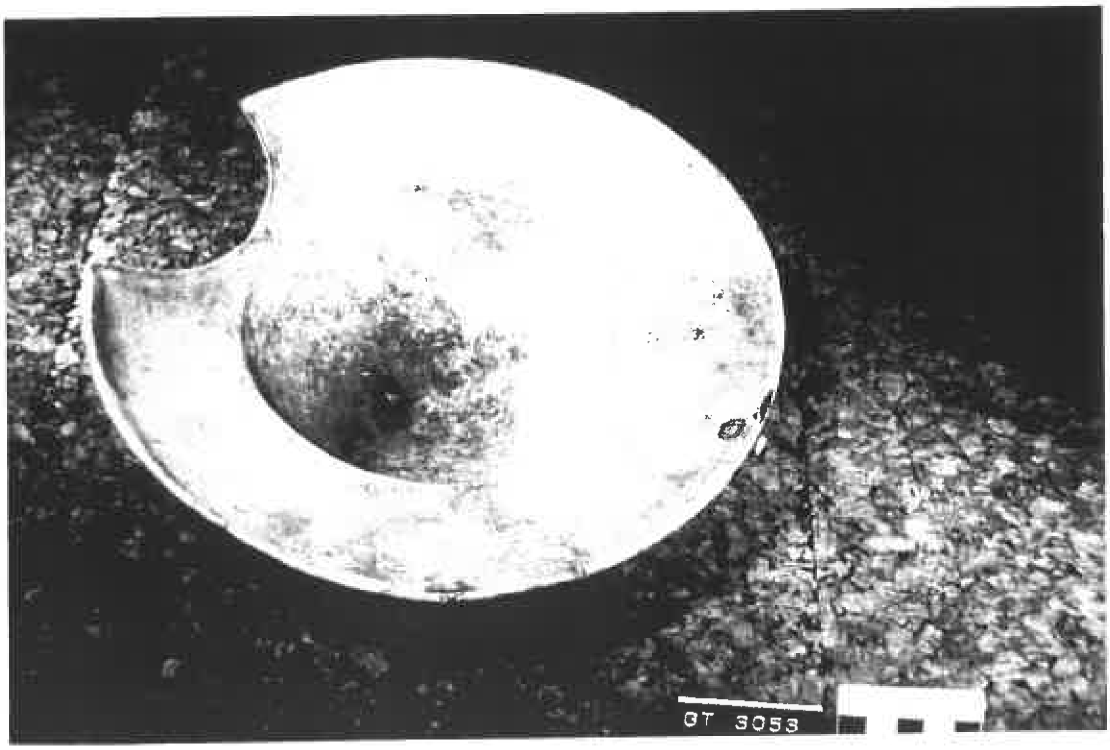


Fig 1b Barber's Bowl - Scale drawing (Side View)

Illustration 1. Barbers Bowl before recovery.

Illustration 2. Barbers Bowl after treatment.



SILVER COINS

Introduction

The bulk treatment of silver coins using sodium dithionite has been discussed in the publication by MacLeod and North 1979.

My first few weeks at the maritime museum were spent cleaning silver coins after their hydrochloric acid wash, ready for this reduction procedure.

Several sets of coins were completely treated but my main activity was with the later stages of the method.

Before treating many of the coins the final removal of silica residues and silver sulphides was necessary. This was not always easy as many of the coins were almost completely corroded away and had the strength of damp biscuit. Iron concretions were often impossible to detach from the fragile mass and required at least one reduction prior to mechanical removal. After a reduction the bonding of the iron corrosion product was weakened and it could usually be prized or gently tapped off. Occasional silicious concretions containing copper were found. These were completely resistant to any chemical agent and intimately bonded to the metal remains. If they could not be fractured off by tapping the only alternative available was to carefully abrade them away with a dental drill and silicon carbide tip.

The reason that passive and protective concretions were removed was not merely cosmetic but necessary if the dithionite solution was to reach the corroded silver beneath. After any such removal was effected the coins were retreated in sodium dithionite.

During some treatments it was found that the coins had not been fully reduced. This may have been due to an improper seal on the container. Plastic sample jars of approximately 500ml capacity were used and the snap on and twist lids were not totally reliable.

When oxygen is able to enter the container the dithionite reacts with air and is quickly oxidised to thiosulphate and an assortment of other oxy-sulphur species up to sulphate. The effective redox potentials of such solutions is unsufficient for useful reduction of the silver corrosion products. These coins were retreated.

After treatment many completely corroded coins had a surface which was composed of a loose network of adventitious silver in which the markings of the original surface were discernible. These were kept in this state and any polishing was by hand in order that the loosely adherent detail was not lost. After all, the reason for the treatment was not to produce a mass of shiney silver but to enable historical details to be recorded.

Infrequently a completely corroded coin gave a final result which did not appear sound. These coins had a dull appearance and were not improved by polishing. An examination of one of them was undertaken using a scanning electron microscope and it was found that no corrosion products remained and the surface was solely silver. A photograph of the surface in question can be found following page 63.

Finishing

The coins had been polished using a glass fibre brush in a glove box. This removed much of the thin layer of grey silver which coated the coins and some of the black silver sulphides. However, it was time consuming and not very safe; rounding off the lettering and other raised details on the coins.

A new process has been devised using a tumbling machine and a mixture of sawdust, kerosene and a small amount of fine grade aluminium oxide polishing powder of less than 0.1 um grain size.

This caused less damage to the surfaces and gave a softer finish.

Unfortunately a source of good hardwood sawdust has yet to be found - workshop sawdust collected by filter bag is usually very dusty and often contains metal particles. A fresh supply of raw sawdust from, for instance, a forest timber mill has not yet been acquired and the system is in abbeyance.

In my short experience of this method it became clear that the sawdust will only remain effective for a certain period. When enough silver debris has been incorporated into it the sawdust separates out from the kerosene and forms a hard cake on the sides of the tumbling jar. This is probably related to the size of the wood particles (with wood shavings this is much less marked) and the amount of silver covering them.

After polishing the coins are cleaned of oils and loose dirt and dewatered in acetone or alcohol.

Storage

The coins are stored in cotton drawstring bags in a safe. Anti-tarnish cloth has been acquired for evaluation as a material for storage bags and for display purposes.

This material is impregnated with fine particles of elemental silver thus filtering off sulphides in the air passing through the cloth.

Investigations

Two sets of coins which had already been deconcreted were used to examine the process in more detail.

These coins were from the "Verguide Draeck" wreck site and were known to have a composition of approximately 94% silver, 6% copper.

A summary of the procedure and accompanying analysis is set out in Figure 2.(pg 16)

Method

The clean, dry but corroded coins were weighed out on a balance to ± 0.01g.

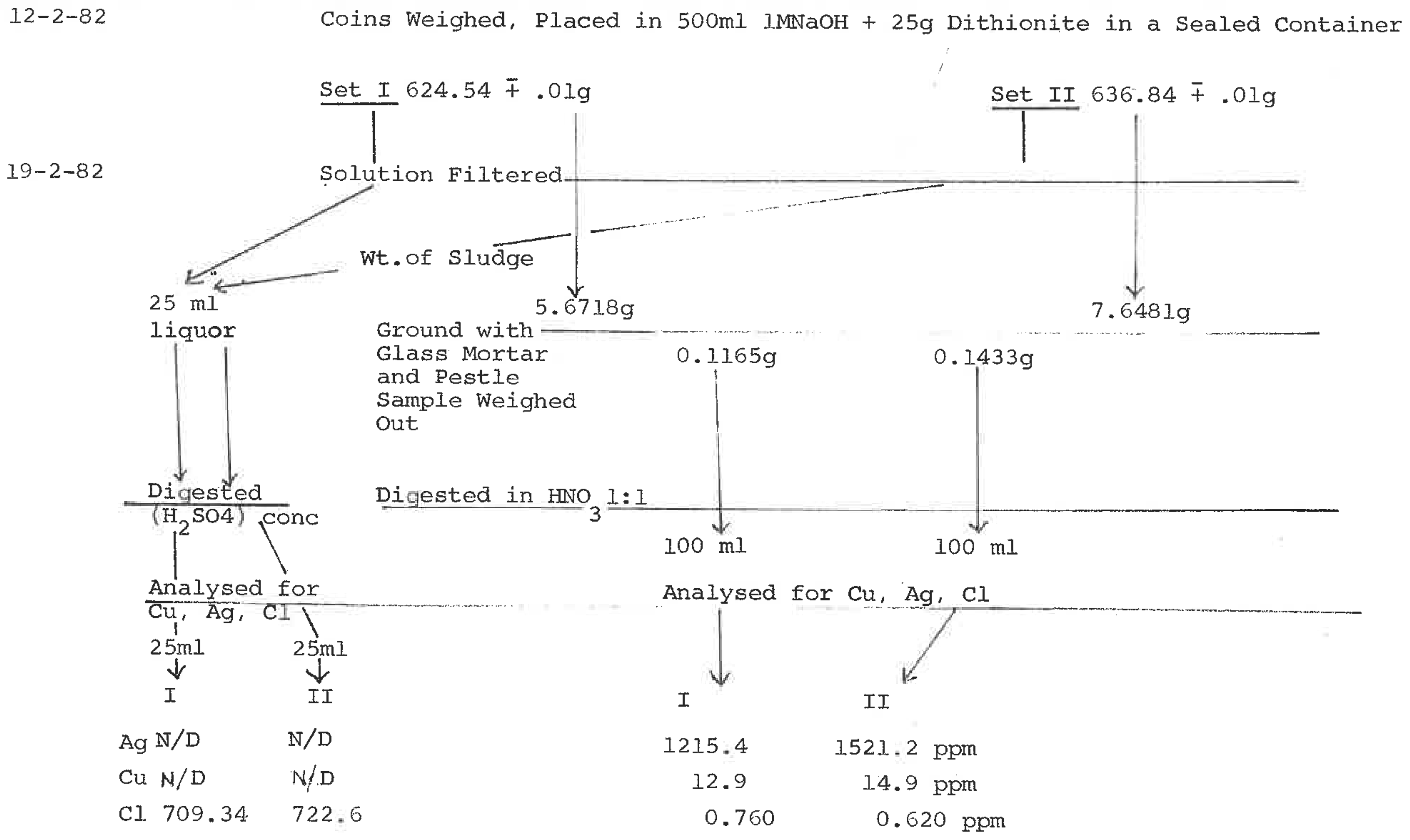


FIG 2. EXPERIMENTAL PROCEDURE FOR DITHIONITE REDUCTION OF CORRODED SILVER COINS

A 5% $^{w/v}$ solution of alkaline sodium dithionite was prepared in a 500ml screw top plastic container using commercial grade sodium dithionite called "Sodium hydrosulphite" and sodium hydroxide (analytical grade) as a 1 Molar solution made up with distilled deionised water.

The dithionite was measured by volume and quickly added to the sodium hydroxide. The coins were immediately placed in the solution and the container sealed and gently rocked in order to dissolve the dithionite. The commercial dithionite has a powerfully pungent odour and so dispensing is done by volume into previously calibrated containers.

The volume of solution added to the container was carefully judged so that an air space did not remain To this end it is well to have a small quantity of the 1 Molar sodium hydroxide to hand in case topping up is required.

There was an almost instantaneous reaction observed in the jars as black silver began to be formed. During the week that the coins remained in solution this increased in quantity and partly flocculated. Quite often a silver and a copper mirror formed on the walls of the container.

The containers were gently agitated each day.

At the end of the week the containers were opened in the fume hood and the fluid poured into a weighed sintered glass filter attached to a water vacuum pump.

The initial liquor obtained was kept for analysis.

The rest together with washing waste from the sludge were exposed in the courtyard and allowed to oxidize to sulphate before being flushed down the drain.

The sludge was washed with deionised, distilled water and finally acetone and allowed to dry over vacuum.

The filter was re-weighed and the total sludge weight obtained by difference.

A sample of sludge was weighed out on an analytical balance to ± 0.0001g and dissolved in 1:1 nitric acid with warming.

The solution was made up to 100ml with distilled deionised water and the volumetric flask wrapped in foil to exclude light. The solutions, liquor and dissolved sludge; were analysed for silver and copper using a Varian AA4 atomic absorption spectrophotometer.

Standards were made up from spectroscopic grade standard solutions diluted appropriately in distilled deionised water using continuous pipettes of 0-20 and 0-100$_{\lambda}^{\mu l.}$ capacity.

A 25ml aliquot of the liquor was further treated prior to chloride analysis.

A 10ml volume of sulphuric acid H_2SO_4 conc. was added to the solution in a 100ml beaker and gently heated in a fume hood. A disproportionation of dithionite occurred and sulphur precipitated out of solution. The solution was reduced to 10ml with much fuming of sulphur dioxide and the solution cleared.

The solution was covered and left to cool. The next day it was made up to approx. 20 ml with deionised distilled water and transferred to a 25ml volumetric flask which was made up to the mark with washings from the beaker.

It was analysed for chlorides on a Buchler Cotlove chloridometer.

Discussion of Results

It can be seen from the results obtained (Table 1) pg21 that the reduction of silver corrosion products went to completion and no silver or copper ions were left in solution.

The chloride produced (355mg and 361mg for samples I and II respectively) was found almost entirely in the solution and represents approximately 0.05% of the total weight of the deconcreted coins treated.

The molar ratio of sludge recovered (98% Ag) to chloride removed during treatment does not indicate that silver chloride was the main corrosion product left on the coins. However, some silver will have been produced from reduction of silver sulphides and some from bromian silver chlorides. Also, the outer corrosion layers of silver coins contain a large percentage of metallic silver as can be seen from one example of corrosion composition shown in Table 2. pg22 The silver present in a matrix of AgCl, Ag Cl/Br is dislodged along with silver formed during the reduction process.

Sample I	Ag	Cu	Cl	Mole Ratio Cl (Liquor)/Ag (Sludge)
(a) Sludge	98.1	1.13	.063%	0.18
(b) Liquor	N/D	N/D	6.25%	
Sample II				
(a) Sludge	100	1.06	.043%	0.14
(b) Liquor	N/D	N/D	4.72%	

TABLE 1

ANALYSIS OF SAMPLES I AND II;

VALUES EXPRESSED AS PERCENTAGES OF Wt OF SLUDGE

Elemental Analysis	Distribution
83.89% Ag	0.0448% AgCl, 57.51% Ag_2S, 26.32% Ag^o
5.85% Cu	0.73% Cu^{II}not S, 4.12% Cu_2S, 0.146% CuCl, 0.85% Cu_2O
1.48% Cl	0.11% AgCl, 0.052%
7.92% S	7.10% Ag_2S, 0.79% Cu_2S, 0.028% S^o

TABLE 2

CORROSION LAYER ANALYSIS OF SULPHIDED SILVER COIN -

(DATA FROM COLLECTION OF I MacLEOD)

The high silver to copper ratio compared to the original composition indicates that corroded copper was removed from the coin during deconcretion, as expected. Copper is preferentially lost from the alloy during corrosion in sea water and green stained concretions on silver coins are often seen.

Conclusion

The use of sodium dithionite for treating silver recovered from marine sites is particularly effective. Because the corrosion products held beneath the concretions retain the surface details of the coins their reduction with concomitant coin stabilization yields much information which would be lost using conventional stripping techniques. As such coins carry dates, mint stamps and their transport was often recorded they can be a valuable item in identifying wrecks.

Because hydrogen evolution is not a problem the laminated nature of the corrosion layers is not disrupted.

As coins can be treated in bulk and the process is not labour intensive alkaline sodium dithionite is an ideal treatment for a museum laboratory with a minimum of staff and equipment.

Attachments: Illustrations 3 and 4 Pre Conservation pg 24, 25
Illustrations 5 After Conservation pg 26

Illustration 3. — Silver coins before recovery.

Illustration 4 - Silver coins before conservation
Note the different concretions on the coins.

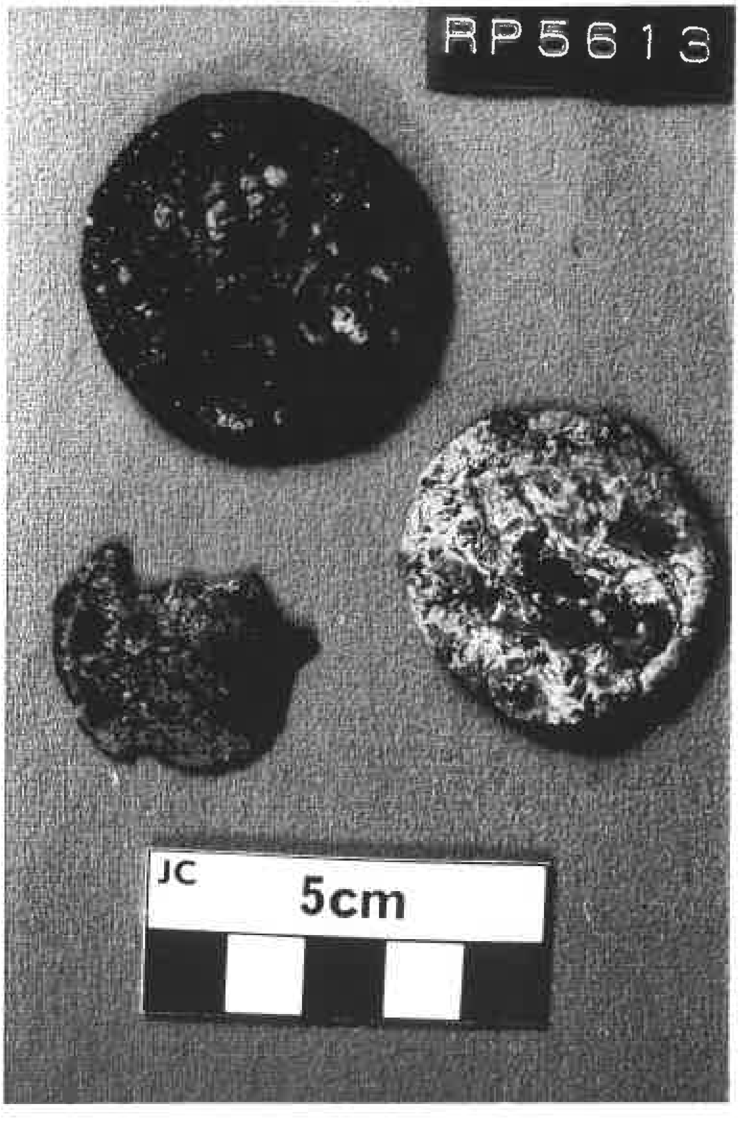
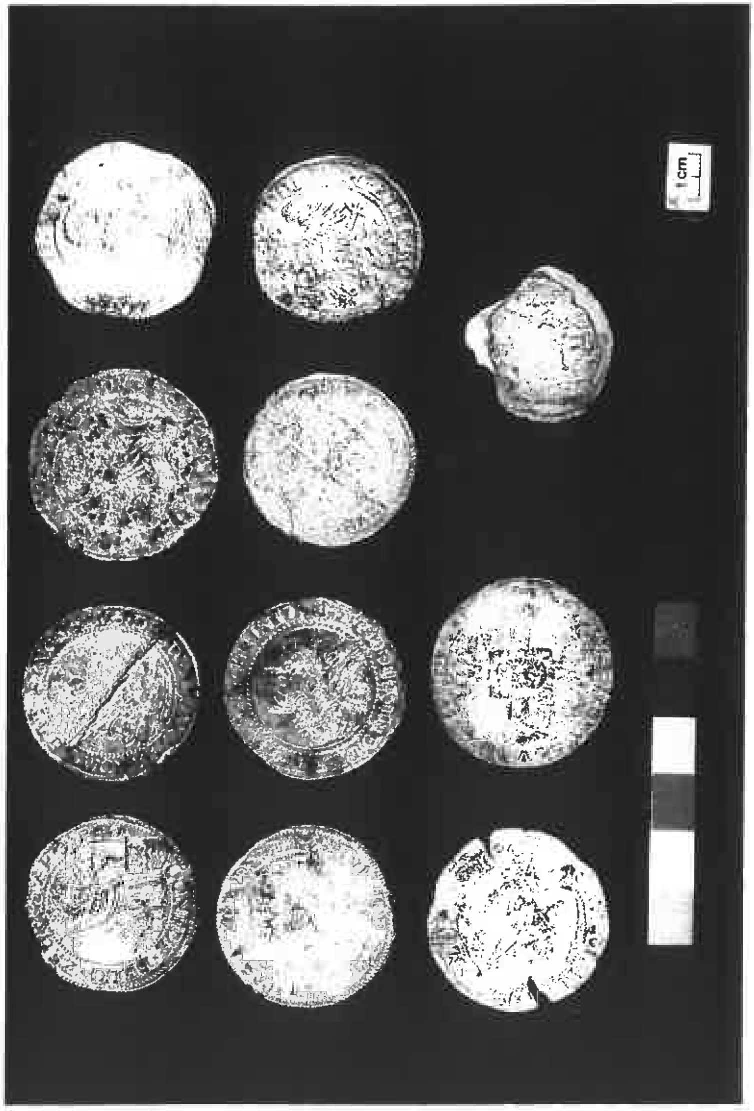


Illustration 5 - Selection of treated
"Batavia" coins. - 1979.



BRONZE PINTLES AND GUDGEON

Description

Four bronze pintles and one gudgeon from the wreck of the "Rapid" (1811). Reg. numbers 5348 (pin) 5348 (gudgeon) 5349, 5350, 5351.

The dimensions, weights and surface area of each item are set out in the attached table 3. pg34

The bronze pivot pins have been broken off two of these pintles. One remaining pin is bent and deeply cracked at its junction with the pintle arms.

Extensive corrosion has occurred over the surface and the metal is porous. Some areas are deeply etched making the grain structures and flow lines acquired at casting clearly visible. (illus. 7) The letters J. DAVIS are visible on the arms (illus. 8).

History and Previous Conservation Treatment

These pintles were recovered from the "Rapid" in February 1980 and treatment commenced in September 1980.

Concretions were removed mechanically using a flat hammer then in 5% w/v citric acid containing 0.5% w/v thiourea and washed for a total of 11,067 hours in 1% w/v sesquicarbonate with the removal of 88.7g of chloride.

During this treatment they acquired a heavy blue green coating of basic copper carbonate which was removed after 155 days of washing.

It had been decided that the pintles would be restored to a lightly oxidised bronze shade since this would match the patina of the "Rapid" rudder gudgeons recovered and treated in 1979/80.

Analysis

An analysis of a metal sample of RP5348 was done in 1981 giving 91.84%Cu, 1.91%Pb, 0.3%Zn, 4.78% Sn n.d. Fe, 0.16% As, 0.12% Sb.

Trial Treatment

The smallest piece, a gudgeon (RP 5348) was immersed in Alkaline Rochelle salt solution (ie, 125g of sodium potassium tartrate added to each litre of 1.75% sodium hydroxide.

After two hours the gudgeon was removed and scrubbed down with a bristle brush. It was replaced in the Rochelle solution until the next day. A large amount of red brown cuprous oxide covered the surface as a loose sludge. This was removed by scrubbing and the gudgeon was well washed in running water for several hours. It was then allowed to dry in the sunlight to ascertain its surface colour.

This proved to be a mixture of olive green and brown shades dulled by a layer of whitish material trapped between the rough grains of the metal surface. When the colours of the metal were saturated this film was no longer seen.

The gudgeon was treated with a 3% w/v benzotriazole solution in 1:1 alcohol/H_2O for two days, allowed to dry out and lacquered with "Incralac"* by brushing.

The appearance achieved was quite pleasing despite the rough surface and was not noticeably shiney.

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* Wattyl product

However, lacquering did not, in my opinion constitute a useful treatment for such a porous surface being unlikely, using a brush application technique, to form a continuous coating. Because of the deeply corroded and subsequently microporous nature of the metal the benzotriazole film would be unlikely to remain protective for more than a few months. On the basis of previously observed failures of this treatment an alternative scheme was devised.

It was decided to use a wax consolidation treatment on these objects and the gudgeon was therefore cleaned of lacquer in an acetone bath.

Treatment

The other pintles were removed from the 1% w/v sesquicarbonate wash solution and after stripping in alkaline Rochelle salt solution, scrubbing and washing as previously described; they were placed in a 3% w/v benzotriazole solution made up with industrial ethanol (97%) and deionized water in equal volumes.

This solution was made up outside in a large polypropylene tank, mounted on a pallet. The barrels of alcohol were rolled up a heavy plank, balanced on the edge of the tank and allowed to drain into it. The deionized water was supplied from the large scale automatic deionizer through a garden hose. A quart size ice cream container of benzotriazole (Copratec 99) was added to the solution and stirred in with a paddle. A face shield, rubber gloves and laboratory coat were worn throughout the operation.

When the pintles had been immersed in the tank it was covered with planks and black plastic sheeting to minimise evaporation and ingress of airborne salts (the sea is within 50 metres of the conservation courtyard).

The bronzes were removed from the benzotriazole solution after three days, dried and transported to the Elders stores nearby to be weighed on their large capacity scales.

Measurements of the external dimensions of the pintles were also made so that a good estimate of their surface areas could be calculated.

The apparent depth of the corrosion layer on the arms of each pintle was measured and the difference between the surface which had been in contact with rudder wood and that free to the sea noted. These measurements will form part of the ever accruing data on relative corrosion rates of different alloys recovered from W.A. waters.

Protective Coating

The pintles were immersed in molten microcrystalline wax (M180) in a wax bath for twenty-four hours and partially cooled in the bath in order to retain the wax in the outer porous layer and thus consolidate it.

At the first attempt at this task the pintles, gudgeon and a pump spear were immersed attached to several thicknesses of twine. When the time came for their removal one pintle was found to be stuck in the fast solidifying wax at the bottom of the bath.

When attempting to lever it out of the bath one operator was burnt when hot wax ran into his gauntlet. The pintle was retrieved but the accident meant that excess wax was not cleaned off the objects while it was still in a molten state.

The two smaller pintles and the gudgeon were cleaned of excess wax with white spirits and bristle brushes of various sizes. Absorbent cloths were used to quickly soak up the surface wax/white spirits so that the deeper layers were not disturbed. Dental picks were needed to remove excess wax from surface pits. Although a pleasant enough finish was obtained the work was time consuming (16 man hours work per object).

Also it was impossible to prevent the incorporation of broken off bristles and dust into the wax coating.

A wire basket capable of carrying the weight of all the pintles was made up by the conservation workshop and the pintles retreated. A fork lift with a set of lifting chains was used to lower in and the next day raise the pintles. As an extra precaution the pintles had been tied to their basket with soft fencing wire. After a few minutes draining they were cool enough for excess wax to be wiped off with a lint free absorbent cloth. No further treatment was necessary.

The pintles were reweighed so that an estimate of the wax used and thus the void volumes could be made.

The Elders' balance only weighed to ±0.100 kilos and the changes in weight of these bronzes after wax impregnation was minimal (see table 3) pg 34. They look neither shiney or waxy, they were a pleasant olive bronze. The heavy metallic mass of the objects is readily apparent and this is most important since it has now been proposed that they form part of a reconstruction of the "Rapid" rudder.

TABLE 3

DIMENSIONAL DETAILS OF PINTLES

						Surface Area Calculations *					
	Weight (kg)	Weight After Wax Treatment (kg)	Maximum Width cm	Maximum Length cm	Maximum Height cm	Av Width of Arm cm	Av Ht of Arm cm	Length of Arm cm	Av Diam. of Pin cm	Ht of Pin cm	Surface Area cm^2
RP 5348 (Pintle) 4 hole	21.6 ∓ 100 g	21.8 ∓ 100 g	30.5	570	29.75	3.36 (+ends 1.87 x 6cm)	6.38	57.0	6.34	23	2732.8
RP 5348 (gudgeon)	12.8 ∓ 100 g	12.9 ∓ 100 g	30.5	25	66	av ht 6.25	circumference 136.6		top and bottom S/A estimated from weighed paper pattern = 610 cm^2		1463.8
RP 5349 7 hole	39.1 ∓ 100 g	39.1 ∓ 100 g	24.4	100	37.2	2.88	7.27	1.55	7.47	29.8	7057.13 +175 *
RP 5351 broken pin 5 hole	26.4 ∓ 100 g	26.4 ∓ 100 g	28.0	89	7.45	2.67	7.01	96.5	(est) (7cm)	-	3736.5 +156 *
RP 5350 broken pin 5 hole	22.4 ∓ 100 g	22.4 ∓ 100 g	30.5	75	7.61	3.38	7.41	75	(est) (7cm)	-	3255.6 +156 *

Density of M180 wax = 0.87 g/cm^{-3}

Upper estimate of void 5348 (a) pintle $230cm^3$

(b) gudgeon $115cm^3$

* All holes diam taken as 2cm, and av length at 2 cm.

i.e. 12.5^{cm2} per hole

Note: These two items were not redipped but cleaned by hand.

The pintles are temporarily stored under a plastic sheet in a clean area awaiting photography.

Recommendations for Storage and Display

Although these objects have been treated for chloride removal and are heavily waxed they are still vulnerable to localised outbreaks of corrosion if stored in conditions of recurring high relative humidity. Being waxed and having a very rough surface they will become covered with dirt in a dusty environment.

It is recommended that they are displayed in a covered case. If an open display is recessary a shellac coat will have to be applied over the waxed surface to reduce dust accumulating there.

At any sign of bronze disease seek immediate conservation advice.

Cleaning

It is suggested that when cleaning becomes necessary the bronze can be washed down with white spirit to remove dirty surface wax, allowed to dry thoroughly and retreated in a molten microcrystalline wax bath.

Notes on Treatment

(1) Despite the disadvantage of a heavy coloured patina produced by a prolonged 1%$^{w/v}$ sesquicarbonate wash it is a preferred solution for any copper alloy containing areas high in zinc, tin or lead. The pH of the solution is approximately ten and as it is a buffer this pH is maintained over a long period given a sufficiency of wash solution to object volume. It also provides anions for counter diffusion of the chlorides. The Pourbaix diagram (page 12 - NBS publ 479) clearly indicates that pH10 is the most satisfactory to use for a prolonged chloride removal treatment.

(2) The chloride content of Perth water is such that deionized water must be used to make up all solutions used for washing. Tap water can be used only for preparing deconcreting solutions but not if chloride, copper and other ionic species removed from the object are to be determined.

Alkaline Rochelle Salt

This stripping agent has a pH of 13.60 and will according to Merk (1978) cause etching of exposed leaded tin bronzes in the presence of corrosion products but not (within one hour) of tin bronzes. It was not the intention in this treatment to remove cuprous oxides or achieve a bright metal surface. (but merely to remove the blue "artificial" patina. After the alkaline Rochelle wash no etching was apparent.) The remaining integrity of the metal was partly due to the thick cuprous oxide patina on the objects. Some of this was however removed because of its intimacy with other corrosion products which were stripped off by the Rochelle solution.

The Benzotriazole Treatment

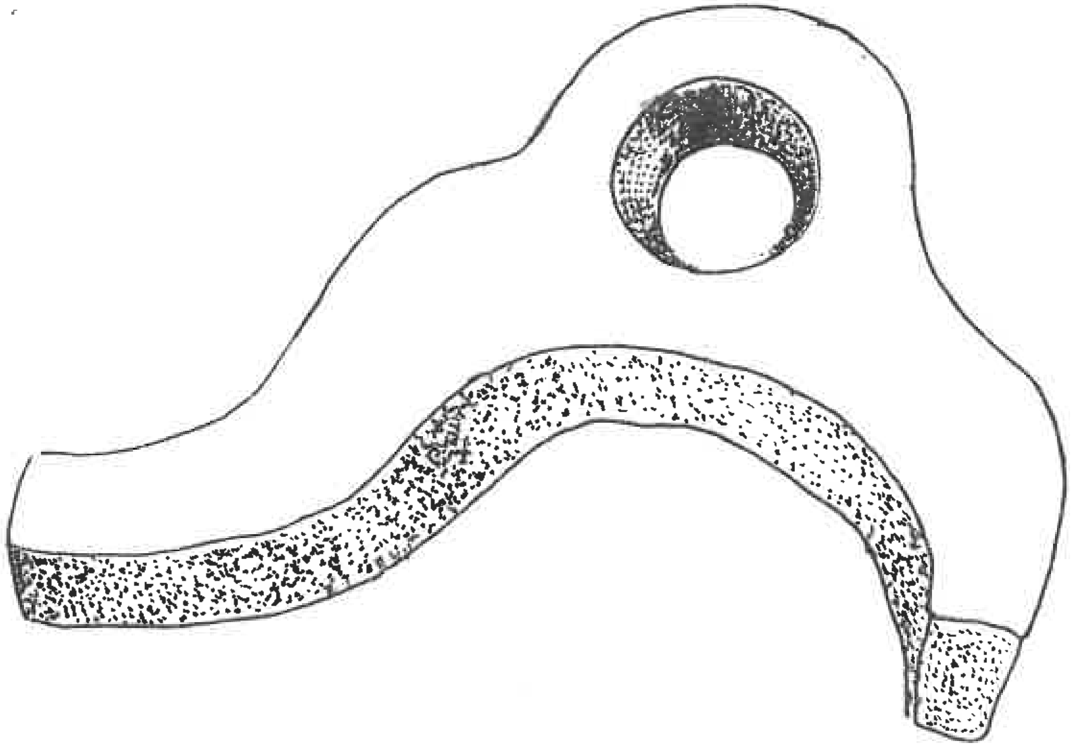
The use of a mixed water alcohol solution is determined primarily by economy. Although a satisfactory concentration of benzotriazole can be obtained in water alone it is higher when alcohol is present. In the mixed solvent system the surface tension of the solution is lower and this allows better penetration into the porous layers of metal. The greatest disadvantage of such bulk solutions is the rate of evaporation even when covered. In this case (it was high summer still) the top inch of a pintle pin became exposed and grew a beautiful 20 cent size spot of bright blue sodium copper carbonate.

This was removed with a swab stick and alkaline Rochelle solution. It was fortunate that a tide mark did not occur. The lesson from this experience is that generous allowance should be made for evaporation when treating objects which are not in a sealed system. Failure to observe such precautions can lead to an inadvertant but pronounced solution line on an artifact which is partly due to the differential aeration of the metal.

Attachments: Figures 3a and 3b. Dimensions of Rapid Pintles and Gudgeon

Illustrations 6, 7, 8, 9. Pintles Before and During Conservation

Fig 3(a) Remains of Gudgeon from Rapid.



Surface Area.

Circumference = 111 cm

av. thickness = 6 cm.

av diameter of central hole = 8·17 cm.

Top and bottom surface area = 610 cm^2
(estimated by weighing paper pattern)

∴ Total area of sides = (25·6 + 111) x 6
= 820·00 cm^2

and Total Area
= 1430·0 cm^2

Fig 3(b) Rapid Pintles – general conformation and dimensions.

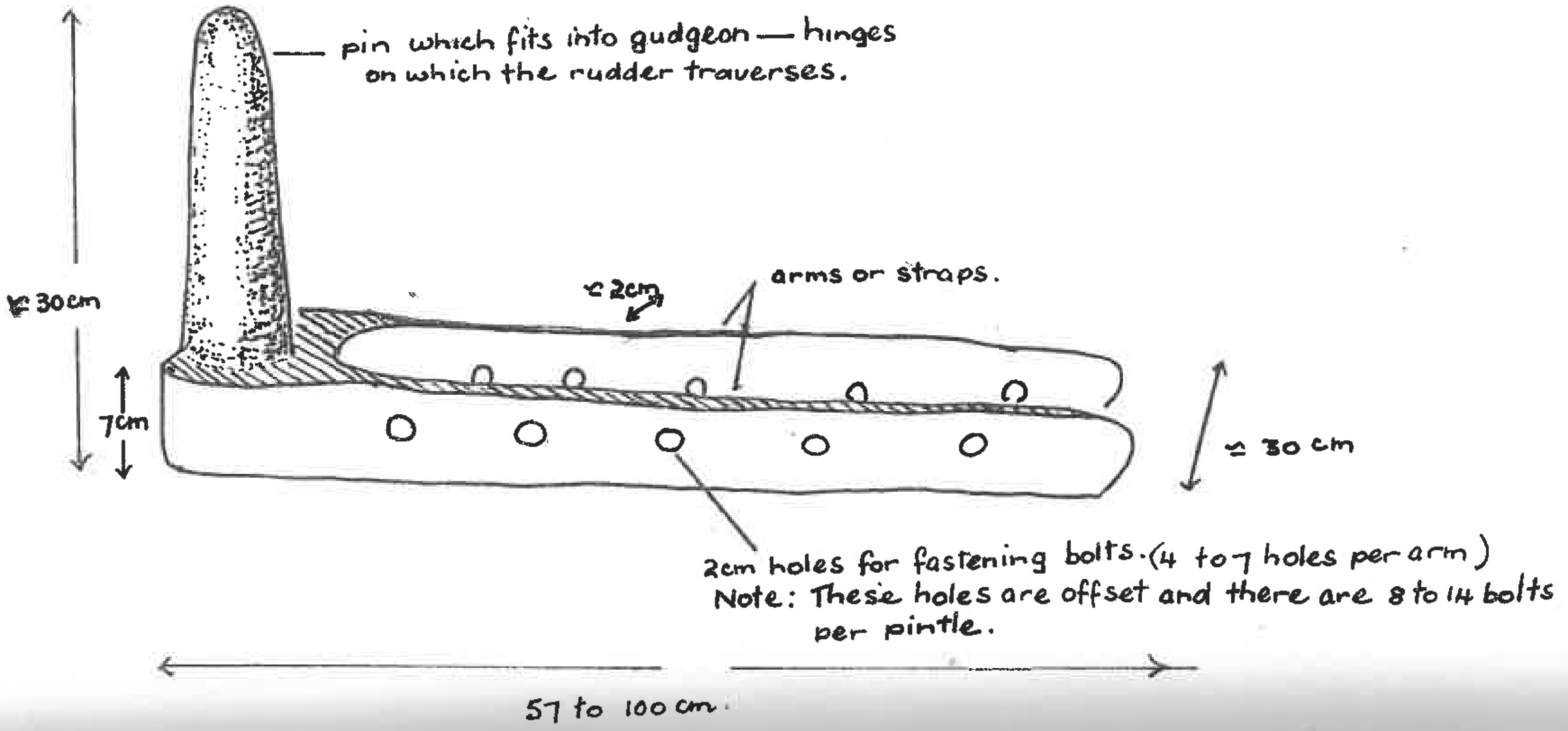


Illustration 6- "Rapid" gudgeon and pintle after recovery before concretion removal.

Illustration 7. Detail of Pintle RPS351 after Benzotriazole Treatment.

Illustration 8. Rapid Pintle during conservation treatment. J. DAVIS. is visible on the pintle arm.

"LEAD" SYRINGES

Acc. No. RP 5631, 5634

Date Received: 5 April 1982

Completion of Treatment: 3 June 1982

Object Description

Three separate finds from the wreck "Rapid" (1811) were recovered in February 1982 which together comprised two antimony containing pewter syringes, the larger 15cm in overall length (plunger in) with an estimated diameter of 2.5cm.

The small syringe consisted of a barrel 7.5cm and a separately found plunger giving an overall length of 9cm with the plunger in and having a diameter of 1.2cm.

Condition on Receipt

All items were heavily concreted with some areas relatively free of any concretion. Wood was incorporated into the concretion about the small barrel. Both syringes were distorted in shape; the large plunger could not be separated from its barrel because of damage occurring at the wreck site prior to excavation.

Illustration 9. Three Rapid Pintles are shown in the foreground; two are without pivots. The Benzotriazole bath is shown on the left.

The effects of 170 years of corrosion were seen after deconcretion and the object must be considered fragile as it appears that one of the intermetallic phases in the pewter had been preferentially corroded.

Evidence of Manufacture

No markings were discovered, however, the direction of cracks and corroded areas suggest that the barrels were made from a spiral of pewter sheet. Both the plungers have a raised line on either side of the shaft suggesting that they were cast from a mould.

Treatment

The syringes were immersed in 5% w/v disodium ethyldiammine tetra acetate, - EDTA - (pH 4.3) for one hour. Gas was evolved from the concretion and outer layers of concretion were shed. It was transferred to a 5% w/v solution of tetra sodium EDTA - (pH 11.5) and remained in this solution for 24 hours. The solution was then renewed and the syringes treated for a further 24 hours. At the end of this time much of the thick concretion had fallen off but it seemed that metal dissolution was occurring at discrete sites.

These areas had already suffered attack from the marine environment.

The remaining concretion was removed using a combination of chemical and mechanical means.

Concretions which could not be prised off the object with safety were softened with local applications of 1-3M hydrochloric acid (HCl) solutions inhibited with one or two drops of concentrated sulphuric acid (H_2SO_4) conc.

A Vibrotool was used to remove some concretions particularly those of greater thickness having wood incorporated in their mass. Loosened and softened concretion was cleaned out of the inside of the syringes using dental tools and finally an inhibited HCl wash.

After deconcreting, the syringes were rinsed in running tap water and allowed to soak in 0.6M sodium sulphate; $Na_2\ SO_4$ - solution for three hours.

They were then rinsed off in tap water and dried with tissues.

The deconcreted syringes had a warty appearance and some of these were quite disfiguring. The mounds were mostly coated with a black layer but were composed of yellow brown powdery material inside. Where it could be seen that these warts did not extend completely through the thickness of the metal they were broken off leaving a circular scar of yellow brown material around an area of roughened or porous grey metal.

These rings were made less obvious by treating with a local application of tartaric acid followed by "liver of salts" - potassium polysulphide.

The final appearance was gratifying; the syringes were recognisable if battered objects. The separately found barrel fitted over the spare plunger. The front surfaces which had faced uppermost on the sea bed were smooth metallic dark grey. The warty areas although still rough blended in with this natural patina. The backs of the barrels showed areas of deep irregular pitting and were not an even smooth black. The syringes were left uncoated for one month. They were then wiped over inside and out with microcrystalline wax in white spirits. Labels were reattached and they were handed back to marine archaeology in an open plastic bag to be stored.

Analysis

Samples were collected for the S.E.M. of corrosion products removed from each syringe, of the wood removed in the concretions and of a complete wart - Results have not yet been obtained.

A small amount of corrosion product was dissolved in HCl (conc) and qualitatively analysed on an atomic absorption spectrophotometer for antimony. There was an unmistakable positive response for this metal.

Display and Storage Recommendations

Store and display this item away from organic vapours. Do not place in wooden containers or in close association with polyvinyl acetates. Avoid handling directly because of:

a. causing the object damage from organic acids in finger prints;

b. the possibility of heavy metal poisoning caused by inadvertently transferring any corrosion products present from hand to mouth.

Discussion

The treatment of lead or pewter objects is complicated by the fact that lead is amphoteric and corrodes in both alkaline and acid conditions. Even in neutral conditions lead can corrode at a significant rate.

The usual preventative measure used to stifle this corrosion during treatment is to add sulphate irons to the system allowing the formation of lead sulphate ($PbSO_4$) on the surface of the metal. The corrosion of lead in high PH solutions cannot be stifled by this means as $PbSO_4$ is soluble in strongly alkaline media. (Lead can corrode in a marine environment if it lacks access to a flow of seawater and therefore sulphate ions.)

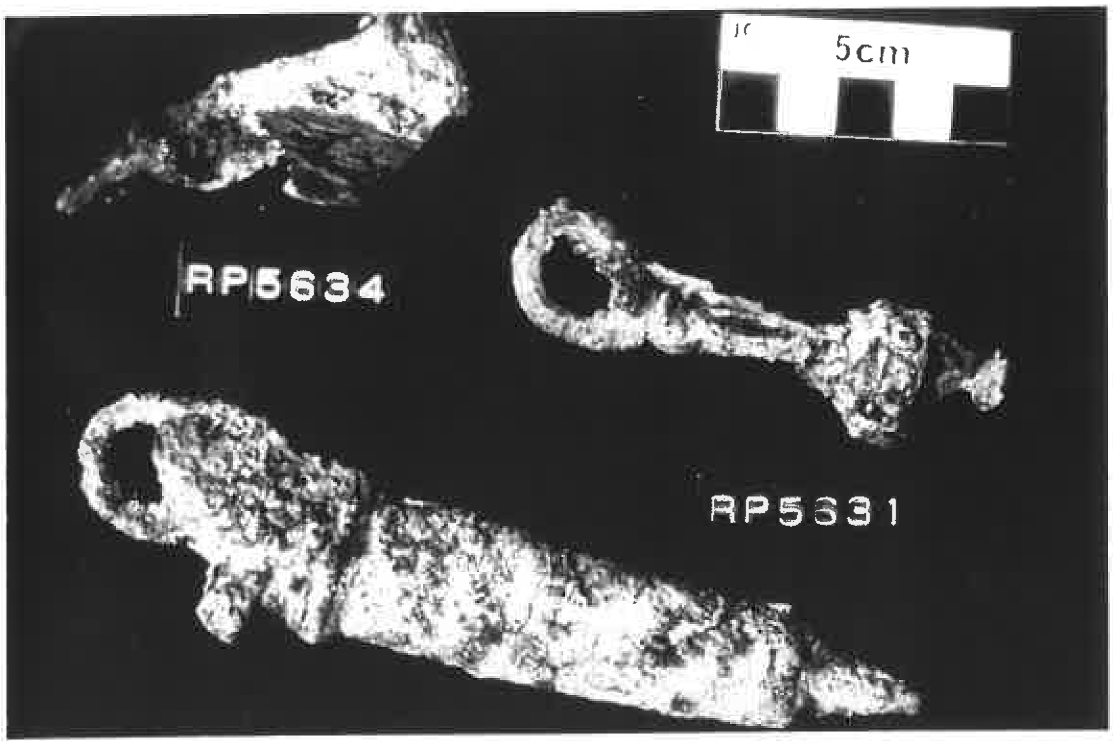
The presence of tin and antimony further complicates the corrosion problem. That a continuous network of tin antimony intermettalic can exist and be cathodic to the matrix has been observed by Campbell and Mills (1976).

Objects which have suffered such effects have little strength.

The treatment of a pewter artifact which has not been fully examined as to metallic structure and composition should be undertaken with caution. Destructive analyses are rarely possible in the treatment of artifacts and the conservator must in most cases rely on documented case histories of similar finds and qualitative analyses of corrosion products.

<u>Attachments</u>: Illustrations 10, 11, 12. pg 52, 53
"Lead" Syringes Before and After Conservation

Illus. 10. Syringes before treatment.



Illust. 11. Syringes after treatment.

Illus. 12. Syringes after treatment
Reverse view; separate parts reassembled.

S.E.M. INVESTIGATIONS

The W.A. Conservation Laboratory is a regular user of the CSIRO Division of Mineralogy's JSM-2 Electron microscope which is set up in the back-scattered electron/low vacuum mode and coupled with energy dispersive X-ray analysis.

The atomic number resolution is excellent especially of polished sections and images can be obtained on a TV screen which give useful information on the composition of samples with several inorganic phases.

As no coating is required for sample preparation and because there is no long wait for vacuum conditions the number of samples that can be processed is far in excess of similar runs on machines using a secondary electron/high vacuum mode.

The main differences between a back-scattered electron/low vacuum method and more usual S.E.M. operations is possible because of:

a. a back-scattered electron detector;

b. a modification to the vacuum system so that a normal high vacuum is maintained in the electron column, while a low vacuum of 0.1 - 0.5 torr exists in the specimen chamber. This means that a sample does not have to be dry and samples of wood and crystals can be scanned without difficulty and without damage to the artifacts.

Powders such as corrosion products can be stuck to double sided tape and examined using high accelerating velocities.

X-radiation originating from areas away from the point of interest must be allowed for when interpreting X-ray spectra. Such anomalies when they occur are usually quite obvious to a reasonably experienced user.

The X-ray facility is designed for the loosely termed "amateur" operator. Instructions are clearly posted in simple sentences on all vital mechanisms and staff are always nearby.

The X-ray diffraction machines are next door and friendly mineralogists are up the hall so the conservator in need of assistance in the analysis of corrosion samples, inorganic pigments or materials does not have far to go for expert advice.

Analyses

(1) pg63 Silver coin referred to previously (pg. 13) giving soft greyish surface after repeated reduction in alkaline sodium dithionite solution.

The EDAX scan gave a result for silver alone. Therefore the phenomenon was morphological in nature and not caused by a failure in treatment.

(2) pg65 After dissolving corrosion products from a copper nail surface using 3 Molar nitric acid and digesting an aliquot of it with sulphuric acid prior to chloride analysis crystallization occurred. The digestion was repeated on a further aliquot but the crystals washed and retained for S.E.M. analysis. Only calcium and sulphur were detected indicating calcium sulphate crystals. The grey area in the photograph is the surface of the double sided tape. This is a good example of a topographical examination which would be well nigh impossible in other S.E.M. set ups.

(3) pg 67 Wood on bronze pintle pin. This is an example of the movement of copper corrosion products in a marine environment. Copper, a trace of chlorine and some sulphur were detected.

(4) pg 69 A higher magnification of the same phenomenon. Copper and chlorine only were detected.
As the copper corroded from the bronze it probably diffused away as copper (I) chloro complexes such as $Cu\,Cl_2^-$ When these species interact with wood they can undergo:

(i) hydrolysis to product cuprous oxide Cu_2O (red brown) A,

(ii) oxidation and hydrolysis to produce copper II hydroxy chlorides such as atacamite $Cu_2\,(OH)_3\,Cl$, B,

(iii) be reduced to elemental copper by wood decomposition products such as formaldehyde (HCHO) or

(iv) interact with sulphides arising from either bacterial activity or degradation processes to produce copper sulphides such as chalcocite (Cu_2S) - C. see pg 68

(4.b) Note the patterns of the cellular components of the formerly present wood retained in the copper corrosion products. (pg 72)

(5) pg 73 Object RP 5337. Copper sheathing in a lead concretion from the gripe lower part of the stem (bow) of the "Rapid". The lead sheathing (4mm thick) was placed over the copper sheathing (1mm thick) to prevent errosion of the copper. The intergranular attack beneath the partly separated concretion layer of carbonates is clearly visible. The overlying lead sheathing is visible in the bottom RH corner, the delaminated European oak of the hull timbers is seen between the concretion and the copper sheathing.

(6) pg 75 A higher magnification of the copper sheet. The lines are from polishing. Note the extent of the intergranular corrosion.

(7) Over view of the "Emden" solder.

pg 77 A sample of this solder was examined by electron probe in the Research School of Earth Sciences, ANU. Lead, tin, zinc and chloride were detected as major components. The lead and tin were concentrated in the central denser areas.

This is a polished section of the same material after electrolysis in 0.6 M sodium sulphate ($NaSO_4$) solution using a stainless steel anode. The pH of the solution fell during electrolysis and the anode corroded severely.

Lead, tin with traces of calcium and zinc were detected.

(8) The same magnification but a different area

pg 79 Lead, tin, chromium and a trace of zinc were detected.

(9) A high magnification of the central area.

pg 81 Lead and tin were detected in high amounts with traces of chromium and zinc. The lighter areas are lead rich while the greyer areas are tin rich.

(10) A closer look at a fretted area (z)
pg83 clearly visible in (8) which borders the lead/
tin rich central area.

The tin phase was reduced compared to lead and no zinc was detected. Once again chromium showed up on the X-ray spectrum.

(11) A high magnification showing more detail of
pg85 the central area of (10). The tin phase was
more evident than lead. Chromium was detected.

(12) A detail of the outer edge of the solder cross
pg87 section gave:

(i) for the finer grained grey area - readings higher in tin than lead. Iron, zinc, chromium and nickel were detected;

(ii) for the dark grey blocks in the upper LH corner. Iron and chromium were the main elements detected with some zinc.

The base of the picture was a mixture of all elements detected with iron and chromium higher than scans taken before (7-12).

The presence of nickel, chromium and iron in this scan was believed to be caused by the coprecipitation of iron corrosion products from the stainless steel which were present in large quantities in the spent electrolysis solution.

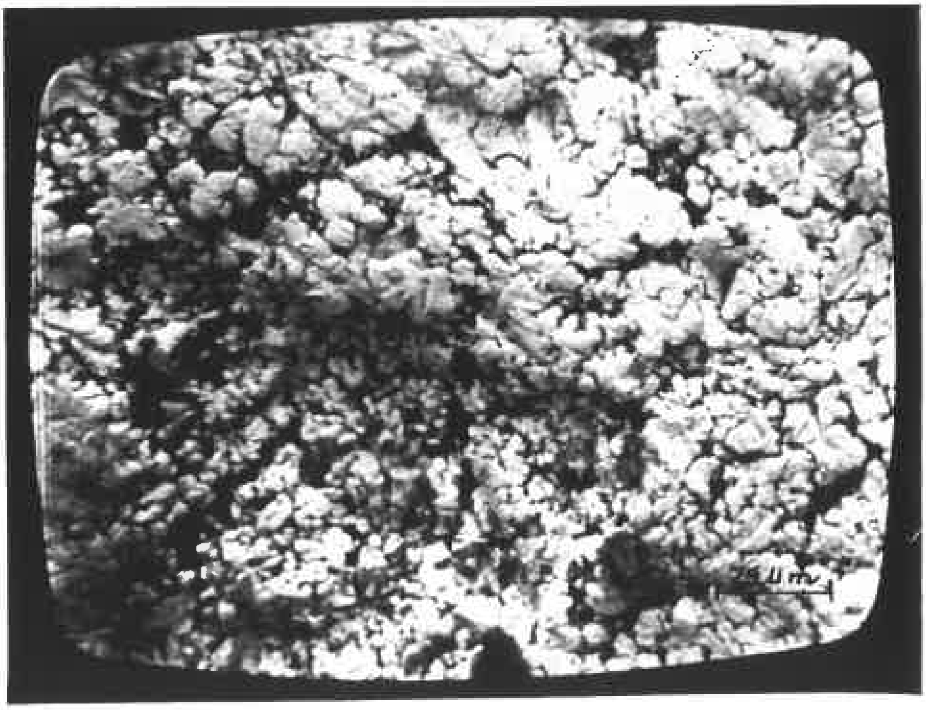
Note: in the following pages f.w refers to the full width of the view depicted. The scale in μm is marked on the accompanying photographs.

ANALYSIS NO. 1

Element detected

FILE 27 / 1-4-82 / NO 8 / x 900 / Ag - "UNREACTED" COIN SURFACE

f.w. 264 m x 10^{-6}



Analysis No 1.

ANALYSIS NO. 2

Elements detected.

FILE 27 / 1-4-82 / NO 1 / x 90 / Ca., S. ONLY

RESIDUE FROM HNO_3 DIGESTION Cu_xS NAILS

f.w. 2643 m x 10^{-6}

Analysis No 2.

ANALYSIS NO. 3

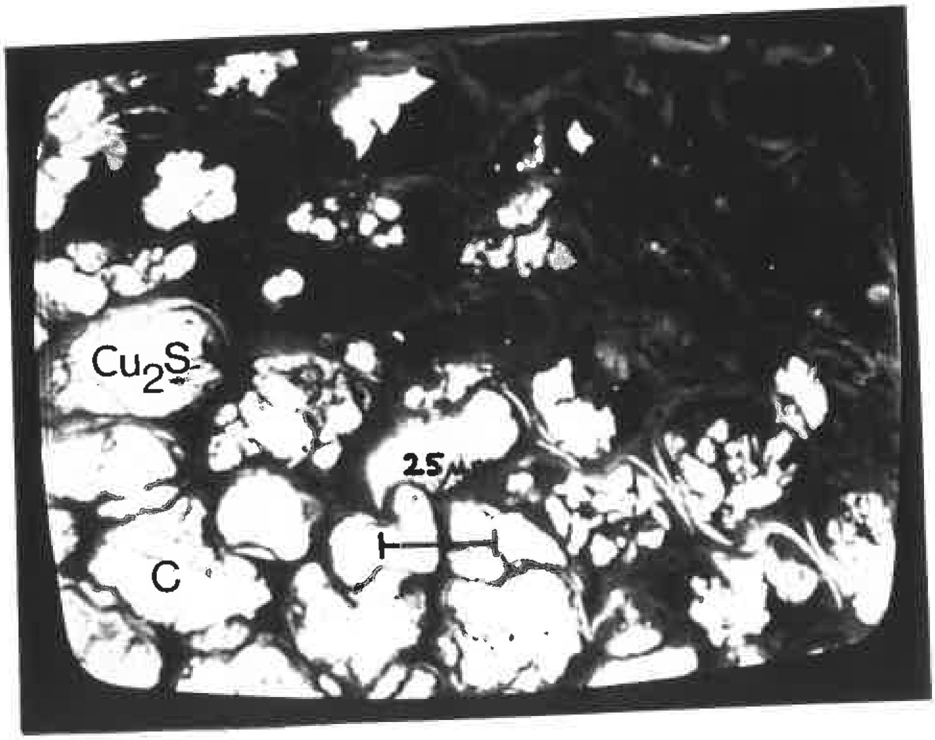
Element detected; count/t.

FILE 27 / 1-4-82 / NO 12 / x 900 / Cu;2983 S;578

SQUASHED WOOD CELL

CONTENTS

f.w. 264 m x 10^{-6}



Analysis No 3.

ANALYSIS NO. 4a

FILE 20 / 3-6-81 / NO 36 / x 350

RATIO Cu/Cl 3.79:1.0

OUTER SEA EDGE OF WOOD FROM ME RUDDER

f.w. 676 m x 10^{-6}

Analysis No 4a.

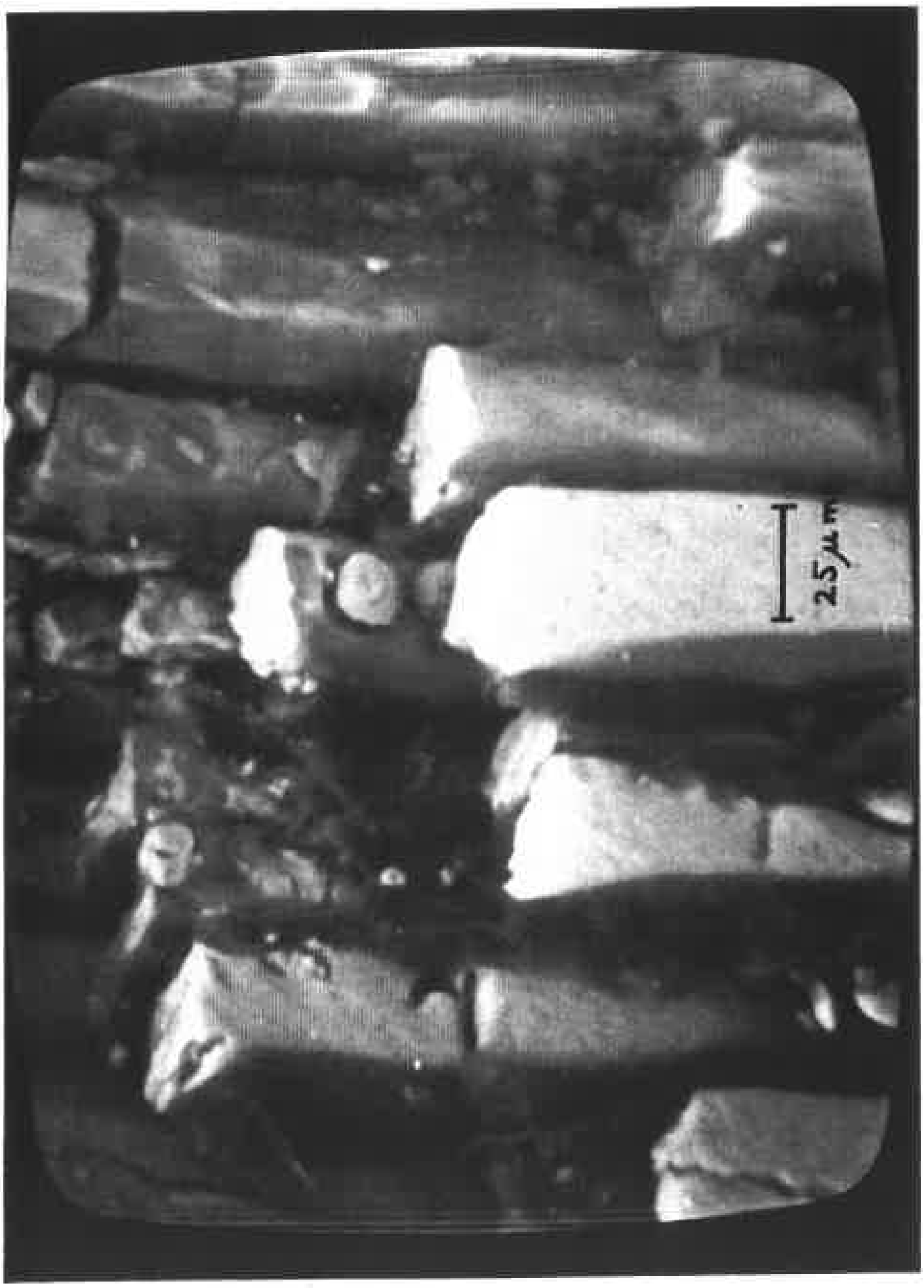
ANALYSIS NO. 4b

FILE 20 / 3-6-81 / NO 35 / x 900 /

RATIO Cu/Cl 3.34:1.0

OUTER SEA EDGE OF WOOD;

ME RUDDER. f.w. 264 m x 10^{-6}



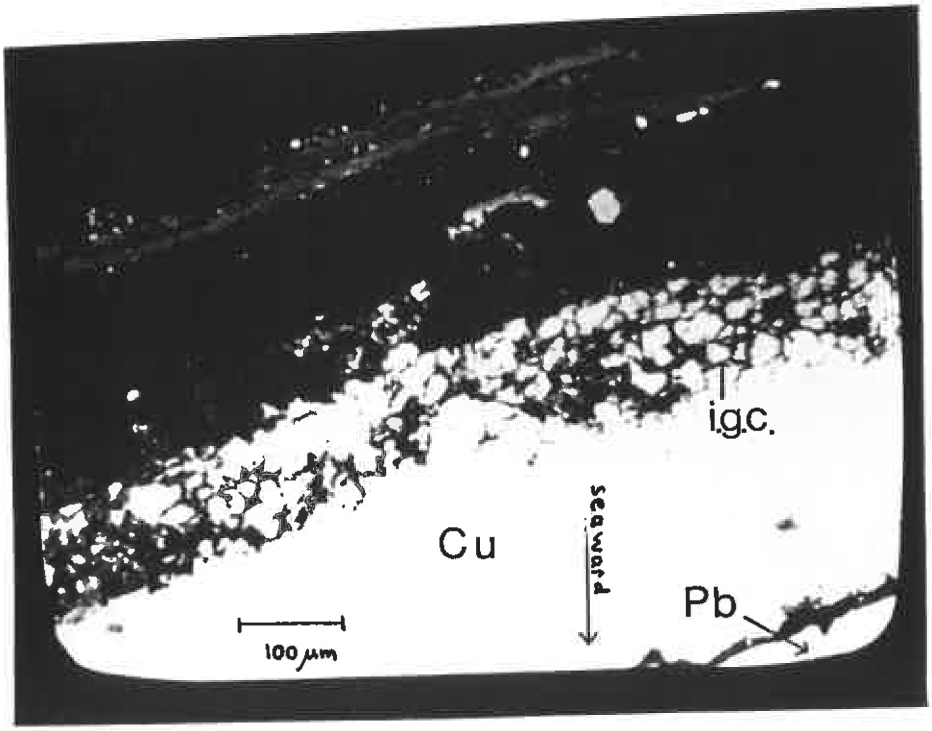
Analysis No 46.

ANALYSIS NO. 5

FILE 27 / 1-4-82 / NO 5e / x 300

Cu SHEET FROM Pb CONC. RP5337

f.w. 793 m x 10^{-6}



Analysis No 5.

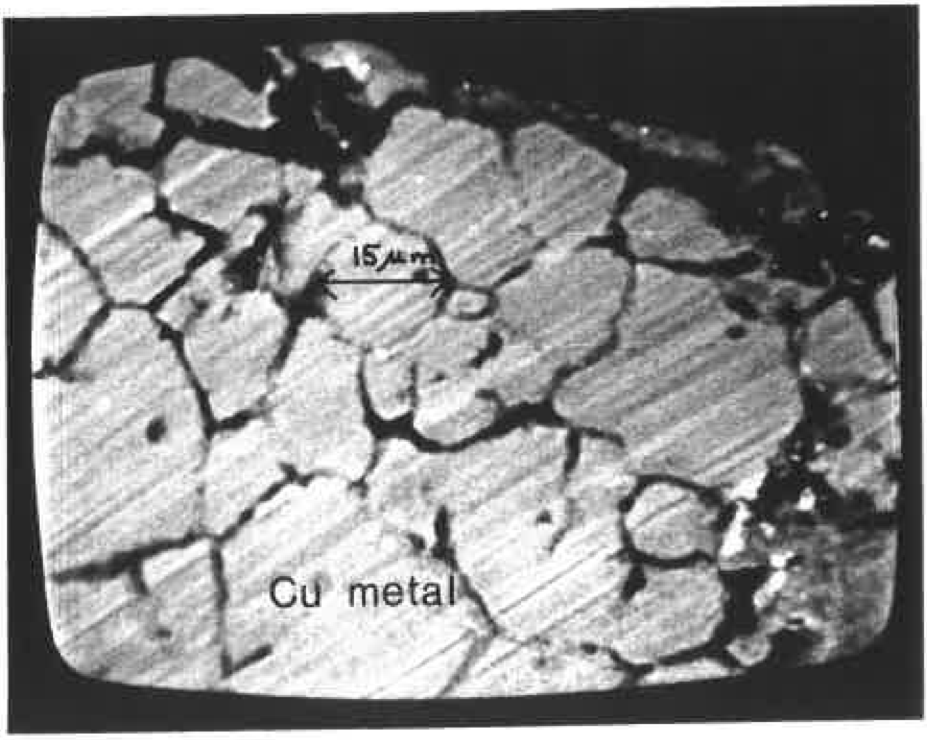
i. g. c. = intergranular corrosion.

ANALYSIS NO. 6

FILE 27 / 1-4-82 / NO 1b / x 2250

Cu SHEET, i.g.c.

f.w. 105 m x 10^{-6}



Analysis No 6.

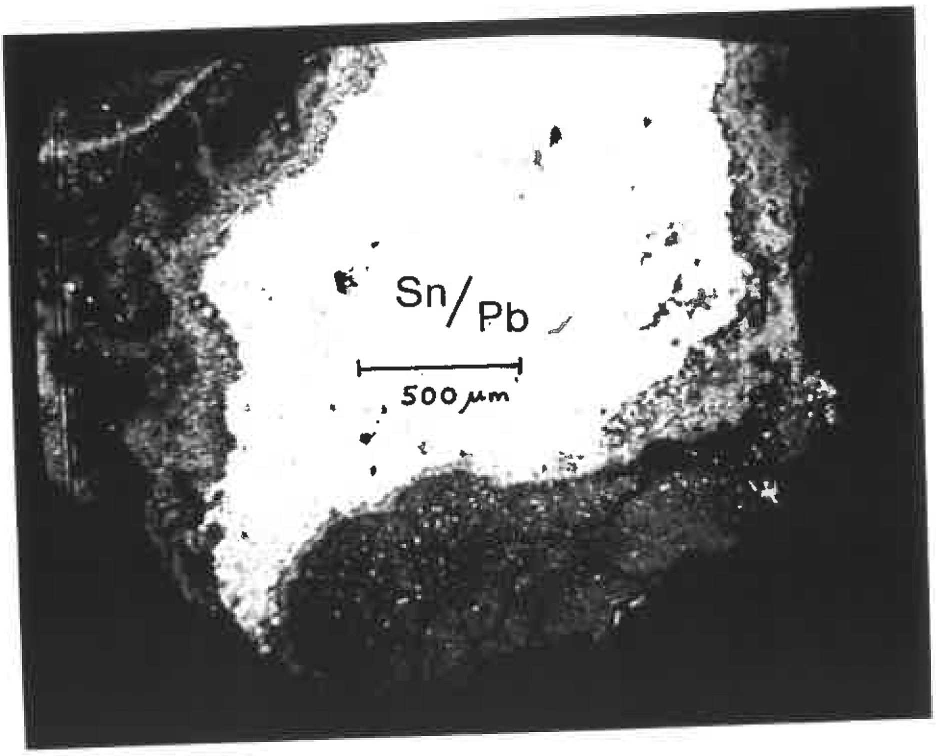
ANALYSIS NO. 7

Elements detected

FILE 27 / 1-4-82 / NO 3 / x 90 / Pb,Sn,Ca (trace) Zn

OVERVIEW EMDEN SOLDER

f.w. 2643 x 10^{-6}



Analysis No 7.

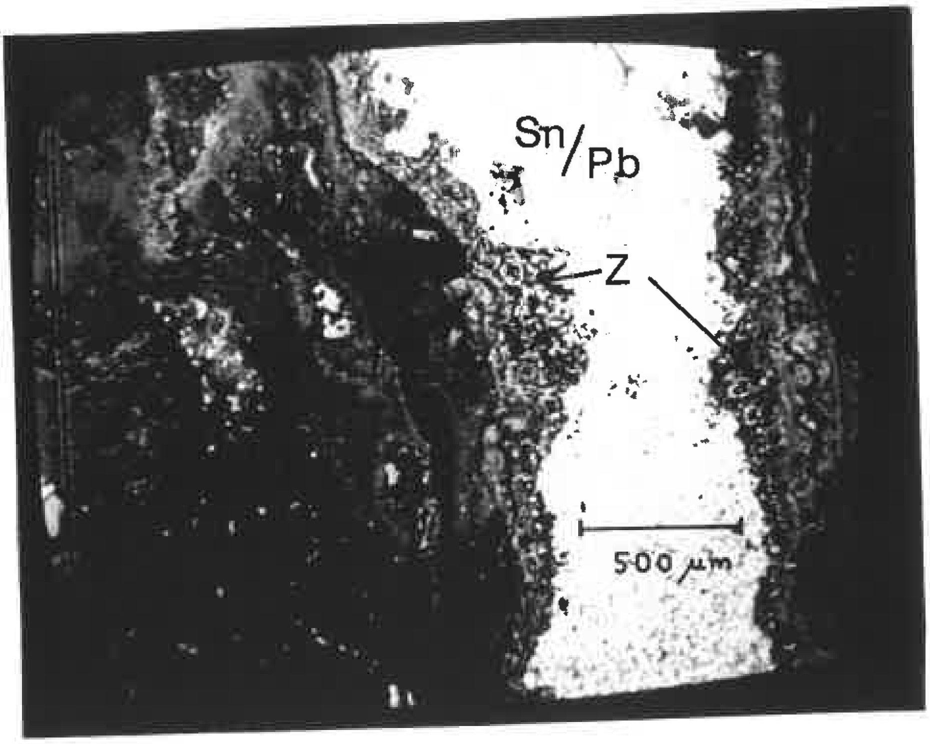
ANALYSIS NO. 8

Elements Detected .

FILE 27 / 1-4-82 / NO 2 / x 90 / PB,Sn,Cr,Zn (trace)

OVERVIEW EMDEN SOLDER

f.w. 2643 m x 10^{-6}



Analysis No 8.

ANALYSIS NO. 9

Element detected; counts/t.

FILE 27 / 1-4-82 / NO 4 / x 9500 / Pb;436, 269, 147

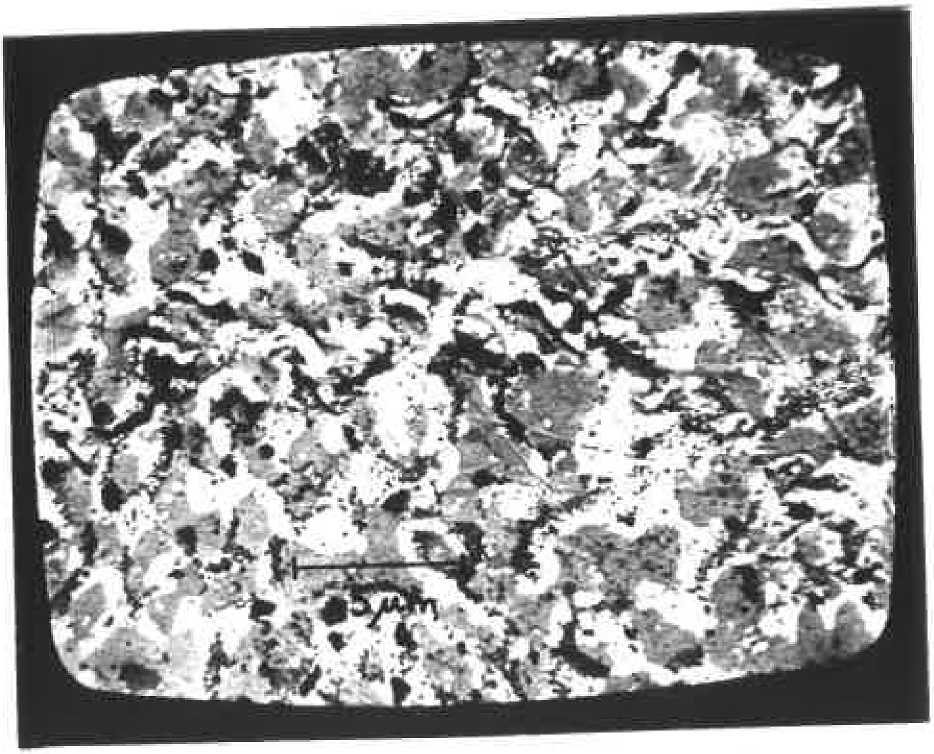
Sn;645

Cr;145

Zn; 80

EMDEN SOLDER. f.w. 25 m x 10^{-6}

note: Pb counts were made at three different points in the spectrum corresponding to three different electron shells for Pb, to confirm the analysis.



Analysis No 9.

ANALYSIS NO. 10

Element detected; counts/t.

FILE 27 / 1-4-82 / NO 5 / x 3000 / Pb;428,235,151

Cr;120

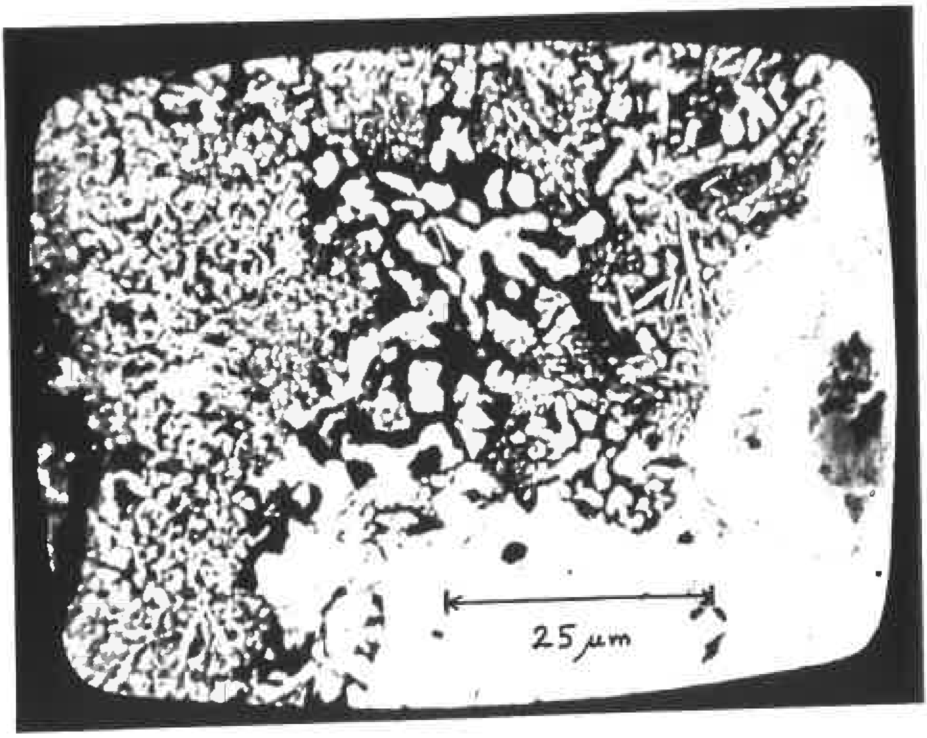
Sn;469

DETAIL OF FRETTED AREA

SOME OF THE PHASES LOST

EMDEN SOLDER

f.w. 79 m x 10^{-6}



Analysis No. 10.

ANALYSIS NO. 11

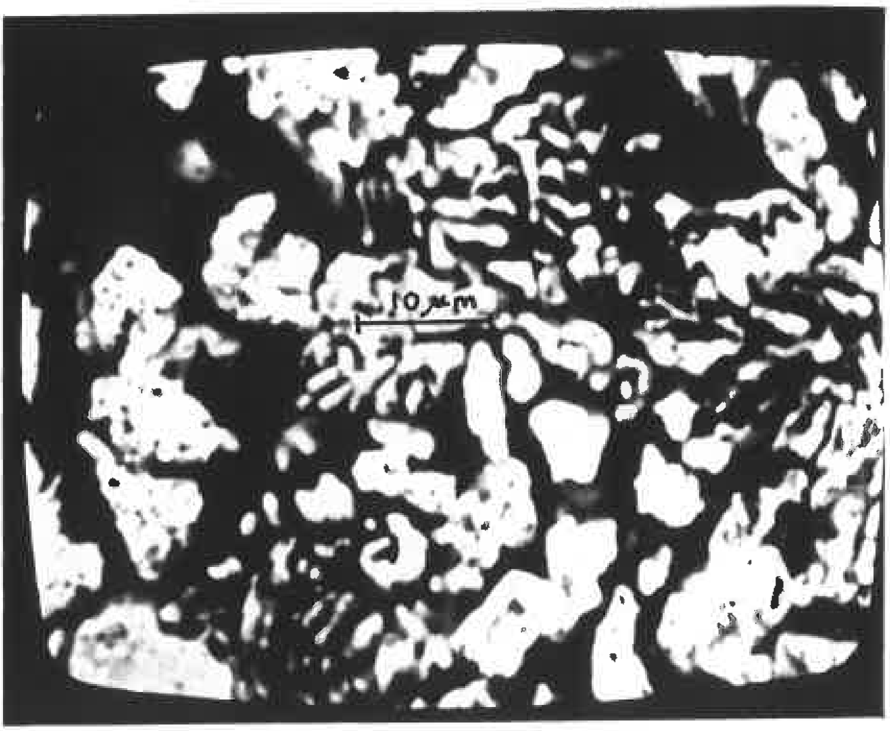
Element detected ; counts/t

FILE 27 / 1-4-82 / NO 6 / x 3700 / Pb;272 126 112

Sn;968

Cr;103

DETAIL ; FRETTED AREA.   f.w. 64 m x 10^{-6}



Analysis No 11.

ANALYSIS NO. 12

Element detected ; counts/t .

FILE 27 / 1-4-82 / NO 7 / x ? /(i)Pb;106,47 (CAULIFLOWER PHASE)

Sn;379

Cr;104

Ni; 46

Zn;393

Fe;241

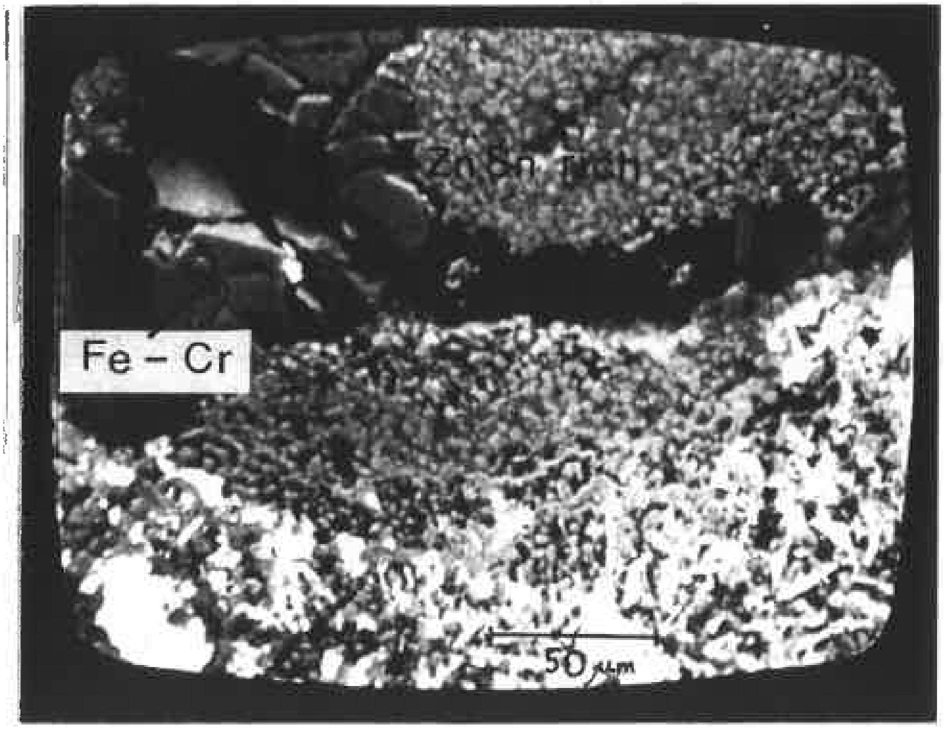
(BULKY BLACK)

(ii) Zn;82 Fe;716 Cr;361

Pb;280,169,80

(BACKGROUND)

(iii) Zn;347, Ni;97 Cr;195 Sn;287



Analysis No. 12.

CHLORIDE LEVELS AND RELEASE RATES ON WASHING FOR COPPER NAILS FROM THE "RAPID"

Background

The conservator does not deal with phenomena allowed expression under controlled experimental conditions, but uses "real world" material which is characteristically hetrogeneous and has been subjected to undocumented variations in the natural environment for a time period not reproducible in a laboratory.

Thus any body of work which goes some way to reconcile real observations with known mechanisms involved in corrosion and its treatment will increase the ability of conservators to monitor such treatments and assist in designing the most appropriate treatment for individual items.

The classification of "copper" objects recovered from the sea by the nature of their concretions is an example of a useful ordering of complex information. MacLeod (1982). The type of concretion indicates the nature of the corrosion mechanism which has occurred and thus the expected condition of the metal beneath.

The standard W.A. Museum treatment for "copper" objects is deconcreting followed by chloride removal in 1% w/v sesquicarbonate solution. Such treatments require a monitoring of chloride concentrations.

Dr MacLeod as the W.A. Museum laboratories is presently collating data on chloride release rates, and in order to increase the data available on anaerobically corroded copper artifacts and to provide myself with practice in chloride analysis and its interpretation I began an investigation of chloride release rates from anaerobically corroded copper nails in sesquicarbonate solution.

The investigation was intended to provide data which could be compared to known release rates from aerobically corroded material of similar composition and age. A comparison of the behaviour of individual nails in the set used was also proposed as data is available which suggests that differences in chloride release rates may be linked to compositional variations in the original alloy. Whether this link is chemical in nature ie, the chloride released is associated with other mobile species such as zinc ions as a complex ion or reflects the microstructural differences of alloy surfaces corroded in a marine environment has not been determined.

No doubt many factors are involved and vary with alloys and corrosion conditions.

The chloride content of corrosion layers was also to be determined.

An anaerobic marine environment is high in sulphide ions produced by the activity of sulphate reducing bacteria which colonize these deoxygenated waters. Sulphide ions react with copper with a localised decrease in pH and formation of copper sulphides.

$$\text{e.g.} \quad 2Cu + HS^- \longrightarrow CU_2S + 2e^- + H^+$$

Continued corrosion favours the formation of copper sulphides and an anaerobic concretion typically consists of discrete phases of sulphides such as covellite (Cu_2S_2) and chalcocite (Cu_2S) and much incorporated material; sand grains, shells and other sea bed detritus. The chloride content of such concretions should be low.

Given the unavoidable experimental error of a simple set up with "real" material no unequivocal answers to these investigations were expected. However, used in conjunction with already determined chloride release rates the results would form a basis for a comparison of chloride release rates from copper artifacts using standard, washing regimes with those using reducing agents such as sodium dithionite. Such a study was begun and forms another chapter in this section of the Internship report.

Experimental Procedure and Materials

Seven nails were selected (as being representative of variations available on anaerobically corroded Cu metal); their weight, average diameter and length obtained and a surface area calculated for each. All nails had been collected from the same areas of the wreck site "Rapid" (1811) and were wrought copper low in tin and lead. Five nails were stripped of corrosion in 3M nitric acid (HNO_3) one (A/5) in alkaline Rochelle solution and one (G/4) left concreted. Nail F/1a had a surface which was entirely rough and covered with small pits. Nail C/2a was worn with rounded edges.

The acid digested corrosion layers were made up to volume with distilled deionised water and retained for analysis. An aliquot of each solution so obtained was subjected to further digestion with concentrated sulphuric acid (H_2SO_4) to remove sulphides. They were made up to a known volume with distilled deionised water.

The nails were placed in covered plastic containers and a measured amount of 1% w/v sesquicarbonate (prepared using analytical grade chemicals and deionised water) was added so that the nails were well covered with solution.

Small volume samples were collected from each solution over a period of time and analysed for chloride and copper ions. The results in parts per million (ppm) were plotted against hours to the half. The volume of the solution was topped up when necessary with 1% w/v sesquicarbonate solution. The solution was renewed when the slope of chloride ion concentration versus $t^{\frac{1}{2}}$ attained a plateau.

The solutions were also analysed for zinc (Zn) and tin (Sn) at several samplings.

The dissolved corrosion products were analysed for copper (Cu), tin (Sn), lead (Pb), zinc (Zn), antimony (Sb), calcium (Ca) and magnesium (Mg). The H_2SO_4 treated aliquot was analysed for chlorides.

At the end of the experiment a sample of metal was obtained from each nail and digested in HNO_3 3M with addition of hydrochloric acid (HCl) (conc) to take up any tin present. This was subjected to compositional analysis.

Chloride analyses were made using a Buchler chloridometer those for metal species by Varian atomic absorption spectrophotometer, (AA4).

Chloride and copper release rates were normalised to weight per unit of surface area per unit of time $^{\frac{1}{2}}$, and compared with one another and the compositional analyses of the relevant corrosion product and metal.

Initial Results

The results are set out in Tables 4, 5 and 6.pg Raw data is contained in Annex 2.

TABLE 4

CHLORIDE RELEASE

S/A (cm^2)	Nail	Volume (ml)	Slope $ppm/hr^{\frac{1}{2}}$	$N_1 \times 10^{-3}$ $mg/cm^2/hr^{\frac{1}{2}}$	V	$Slope_2$	$N_2 \times 10^{-3}$ $mg/cm^2/hr^{\frac{1}{2}}$	V	$Slope_3$	$N_3 \times 10^{-3}$
186.2	A/5	1000	Insuff. Data		1000	1.43 ∓ .25	7.7 ∓ 1.35			
79.46	B/2b	600	Insuff. Data		600	1.61 ∓ 0.38	12.2 ∓ 2.87	1000	0.28 ∓ 0.12	3.5 ∓ 1.50
66.90	C/2a	600	0.24 ∓ 0.04	2.12 ∓ .36	500	1.13 ∓ .22	8.4 ∓ 1.64)			
79.75	D/1b	600	Insuff. Data		500	1.84 ∓ 0.16	11.5 ∓ .99)		Below Measurement	
118.74	E/3	1000	0.12 ∓ .01	1.0 ∓ .083	1000	1.44 ∓ .15	12.1 ∓ 1.26)			
60.55	F/1a	600			600	1.74 ∓ .46	17.2 ∓ 4.55)			
188.7	G/4*	1000	2.21 ∓ 0.16	11.7 ∓ .85	1000	1.82 ∓ .52	9.6 ∓ 2.74	1000	0.04 ∓ .12	
371.84	(ACE)							1000	0.87 ∓ .16	2.3 ∓ .42
63.35	C/aer	500_{H_2O}	0.46 ∓ .09	3.6 ∓ .70	500_{KNO_3}	0.45 ∓ .18	3.6 ∓ 1.44			
65.33	E/aer	1000	0.58 ∓ .21	8.4 ∓ 3.04	500_{KNO_3}	7.01 ∓ 0.50	54.0 ∓ 3.85			

Note: N = the normalised release rate in $mg/cm^2/hour^{\frac{1}{4}}$

Average N for sulphided nails = $11.53 \mp 2.20 \times 10^{-3}$

---

cf Average N for copper objects = $5.6 \mp 2.1 \times 10^{-3}$

TABLE 5

DATA SUMMARY SHEET - Cu RELEASE

S/A (cm^2)	Nail	Volume$_1$ (ml)	Slope$_1$ ($ppm/hr^{\frac{1}{2}}$)	N x 10^{-3} ($mg/cm^2/hr^{\frac{1}{2}}$)	V_2	Slope$_2$	N_2 x 10^{-3}	V_3	Slope$_3$	N_3 x 10^{-3}
186.2	A/5	1000	0.20 $\mp$ 0.08	1.07 $\mp$ .428	1000	0.54 $\mp$ .05	2.9 $\mp$ .26			
79.46	B/2b	Insuff. data			600	0.69 $\mp$ .04	5.1 $\mp$ .31		0.38 $\mp$ .07	4.8 $\mp$ .250
66.90	C/2a	Insuff. data			500	0.73 $\mp$ .06	6.5 $\mp$ .52			
79.75	D/1b	Insuff. data			500	0.45 $\mp$ .05	4.5 $\mp$ .50		0.43 $\mp$ .02	5.4 $\mp$ .250
118.74	E/3		.03 $\mp$ .02		1000	0.47 $\mp$ .04	3.9 $\mp$ .31			
60.55	F/1a	Insuff. data			600	0.45 $\mp$ .05	2.8 $\mp$ .31		0.29 $\mp$ .12	
188.7	G/4		.08 $\mp$ .03	.42 $\mp$ 1.60	1000	0.33 $\mp$ .03	1.74 $\mp$ .160		Insuff. data	
371.84	(ACE)							1000	0.49 $\mp$ .08	1.3 $\mp$ .22
63.35	C/air	500			500					
65.33	E/air	1000	1.81 $\mp$ .20	27.0 + 2.98		Insuff. data				

Av N = 3.72 $\mp$ .34 x 10^{-3}

for sulphided nails

TABLE 6

METAL ANALYSIS of - CORROSION ANALYSIS - CORRECTED VALUES EXPRESSED AS PERCENTAGES

Nail	Cu	Sn	Pb	Zn	Sb	Ca	Mg	Ni	Ag	Cl
A/5	99.32	-	0.33	0.012	0.23	-	-	0.00116	-	-
B/2b	99.67	-	0.15	0.007	0.07	-	-	.00007		
	99.73		0.25	0.003	0.01	0.01	0.01		0.003	1.37
C/2a	99.51		0.20	0.018	0.18			.00033		
	99.26		0.65	0.021	0.03	0.82	0.57		0.044	1.68
D/1b	99.63	0.18	0.01	0.013	0.07			.00068		
	99.94		0.04	0.003	0.02	0.02	0.03		.0018	2.15
E/3	99.46	0.35	0.01	0.010	0.06			.00041		
	99.91		0.049	0.003	0.02	0.56	0.03		0.015	3.11
F/1a	99.49	0.09	0.26	0.006	0.06			.00050		
	98.99		0.81	0.017	0.10	0.33	0.14		0.011	3.42
G/4	99.57	0.24	0.03	0.005	0.05			.00034		
C/2 aer	88.76	9.40	1.20	0.318	0.22			.00081		

The first wash did not yield much useable information as the sesquicarbonate stock solution was contaminated with hydroxide and "topping up" of individual containers caused a rise in pH and a precipitation of ions in solution.

The chloride content of the corrosion products for all nails tested was low compared with data obtained elsewhere for aerobically corroded material of similar composition. The highest value was 3.11%.

The normalised release rate of chloride ion did not differ significantly within the group of nails tested. Results for nail F/1a can be explained as an error in calculated surface area. Its pitted surface would at least double its effective surface area bringing its release rate in line with other values obtained.

Nail G/4 was less affected by changes in pH in the first wash and the N values for wash 1 and 2 are of similar value.

The third wash of all nails used including a combined wash for nails A/5, C/2a and E/3 produced low rates of chloride release. B/2b was the only nail which still exhibited a measurable release rate for chlorides.

The combination of nails A, C and E in the one bath gave a more readable result on graphs plotted and indicates the experimental limitations of monitoring release rates using large wash volumes with small surface areas of artifacts.

The release rate of G/4 was not able to be calculated for the 3rd wash because the release rate was indistinguishable from random experimental error. The values given in Table I and II were calculated using $t_{\frac{1}{2}}$ values whose zero was taken at the commencement of the wash in question. This was done in order to see if a positive slope could be obtained from the data. The data was limited as at the real $t_{\frac{1}{2}}$ values sampling times were too close. A sampling of at least 3 week intervals would be necessary to obtain a satisfactory curve. The level of chloride detected was too high (nine ppm) given the nail's surface area and the volume of the bath for chloride removal to be considered complete.

The Cu release rates obtained of anaerobically corroded copper nails did not bear direct comparison to the corresponding chloride release rates. On average they were $\frac{1}{3}$ the chloride release rates over the same period of time. They did not plateau at the same time as the chlorides. Nails D/1b and B/2b continued to release copper ions after the chloride plateau was reached during wash 2 and continued to release copper ions during wash 3 although chloride ion removal had virtually ceased. It would appear from these observations that copper release is governed by a different reaction to that controlling chloride release.

The comparison of values for metal species in Nail metal and corrosion layers was done by calculating a corrosion ratio for each pair of values. Keeping in mind the inherent errors in the data a corrosion ratio of less than 1 indicated that corrosion had not occurred.

The examination of the Data Table 6 pg 95 suggest that:

a. Lead has been selectively corroded.
b. Corrosion at zinc enriched grain boundaries has occurred in F/1a.
c. Zinc and antimony are associated in the metal.

Such speculations would need to be confirmed by metallographic examination of the artifacts.

The composition of the nails A-G did not vary greatly and it was confirmed that they were low tin lead bronzes. The differences observed may well reflect localised inhomogeneities in the alloy.

Given the apparent error in the N values for chlorides and copper releases rates differences in these values could not be related to their relative metal composition. As the nails were low in metals other than copper this was not unexpected.

Further Experimentation

Nails B/2b, D/1b and F/1a were treated with alkaline sodium dithionite solution in order to ascertain if chlorides had been successfully removed.

Sodium dithionite increases the release rate of chlorides by a factor of 100 and thus remaining chlorides if present would be easily detected in the dithionite wash.

Three aerobically corroded nails had become available for treatment. These were not believed to be of similar composition to nails A to G, or were from the same area of the wreck site. However, it was thought that they might provide useful information on variations in chloride release rates compared to that of copper, dependent on the type of corrosion product present.

Nail 3 was set aside for dithionite reduction. Nail C/2 was mechanically stripped to bare metal and nail E/1 was left untouched.

The surface area of each nail was calculated, and a sample of metal from nail C/2 was obtained at the end of treatment and prepared for compositional analysis. The stripped nail was subjected to a wash in distilled water and when enough data had been obtained to calculate a chloride release rate it was immersed in 0.2 M potassium nitrate solution which provided a counter current for diffusion processes.

Nail E/1 was first washed in sesquicarbonate followed by 0.2 M KNO_3.

Further Results

As set out in Tables 4, 5 and 6 pg 95 the chloride release rates for the stripped nail was not noticeably altered by replacing distilled water with a solution of KNO_3 whose ionic strength did not impede the diffusion of chloride ions. Copper release was low and readings remained steady throughout the first wash and were too low for analysis during the second wash. Zinc was detected in wash 2.

The release rate of chloride in sesquicarbonate for the corrosion covered nail E/1 was comparable to that of the previous batch of anaerobically corroded nails. The release of copper was much higher and was approximately three times the chloride release rate.

The second wash of E/1 in 0.2 M KNO_3 led to a rapid rise in chloride release with a concommitant fall in copper detected in solution. A small amount of zinc was detected in solution.

The dithionite treatment of nails B D and F yielded chlorides which were at the limits of the detection method used. The analysis of the metal sample from nail C/2 gave higher values for tin lead zinc and antimony than the anaerobically corroded set A-G.

<u>Discussion</u>

A 1% w/v sesquicarbonate solution has a pH of approximately 10. At this pH cuprous chloride (Cu Cl) is not stable and undergoes hydrolysis to cuprous oxide (Cu_2O) releasing chloride ions which will diffuse out into the area of lower chloride concentration; the bulk solution.

$$2\ CuCl + H_2O \rightleftharpoons Cu_2O + 2H^+ + 2Cl^-.$$

Counter diffusion of carbonate and bicarbonate anions into the corrosion layer produces more cuprous oxide and basic copper carbonates which can precipitate at a high pH.

The aerobically produced corrosion layer on nail E/1 contained much atacamite $Cu_2(OH)_3Cl$ which at lower pH's breaks down releasing chlorides.

$$Cu_2(OH)_3Cl + 3H^+ \rightarrow 2Cu^{2+} + 3H_2O + Cl^-$$

As basic copper compounds are formed in the sesquicarbonate solution chloride ions held in such complexes will be released with an decrease in the pH of the solution as occurred when E/1 was placed in 0.2M KNO_3. The washing out of the chloride ions into the bulk solution is facilitated by the 0.2M KNO_3 which provides a counter current for diffusion processes and has the same ionic strength as the chloride species held in solution in the corrosion layer. Copper II ions are removed from solution as the oxide or carbonates.

The absence of change in the chloride release rate for nail C/2 when it was transferred from a distilled water wash to 0.2M KNO_3 can be explained in several ways.

Either:

(i) the effect of removing pH gradients and providing anions for counter diffusion is too small to be measured under the experimental conditions prevailing; and/or

(ii) the total chloride levels were so reduced by stripping and the first wash that a pre-plateau phenomenon was being monitored.

Conclusions

Despite the use of "real world" material normalised release rates can provide information on the processes involved in chloride removal from the different types of corrosion occurring on copper artifacts from a marine environment.

It was demonstrated in this limited study that the chloride release rate from anaerobically corroded copper nails in 1% sesquicarbonate was 11.53 ∓ 2.20mg/$cm^2/hr^{\frac{1}{2}}$ which is higher than that obtained for objects having aerobic A type, and cathodically protected B types of concretions. MacLeod (1982) However, the apparent error of all measurements done to date reduces the significance of this result and an examination of all data so far obtained by MacLeod for aqueous washing in air shows that the thickness of the patina or concretion has an insignificant effect on the rate of release of chlorides when compared to non standard regimes.

Objects corroded under aerobic or anaerobic conditions can be treated unaltered if so desired. The length of time such a treatment will take will be considerable as the total weight of chloride ion which must be removed is high. This study confirmed the fact that the percentage of chloride in anaerobic corrosion layers on copper objects is much lower than that in aerobically corroded copper material. Values for the latter can be as high as 19%. As all "copper" stripping agents commonly used in conservation have been found aggressive. Merk (1981) It is suggested that mechanical deconcretion followed by chloride extraction in a suitable washing agent may be less deleterious to many objects.

The practice of stripping an object and then subjecting it to a benzotriazole wash has been found by practice to be an insufficient treatment in many cases MacLeod (1982).

The results of chloride analysis tabled here clearly show that anaerobically corroded nails stripped of corrosion products still contained chloride ion which required 312 hours of washing before its diffusion out of the object could be considered complete. Thus close attention must be given by the conservator to successfully removing pockets of chlorides if a treatment is to stand the test of time.

CHLORIDE EXTRACTION FROM CORRODED COPPER USING ALKALINE SODIUM DITHIONITE SOLUTIONS

Background

Chloride release rates from corroded copper objects have been found to be $5.6 \mp 2.1 \times 10^{-3}$ $mg/cm^2/t^{\frac{1}{2}}$ for conventional washing regimes. Electrolysis is known to increase chloride release rates in both iron and copper, MacLeod and North (9982). but is an awkward technique for bulk treatments of many small objects and it can disrupt fragile surfaces (as gas is evolved).

Some success had been obtained at the W.A. Museum by using alkaline dithionite reduction methods on a few "copper" objects. It was decided to investigate the method in more detail and in particular to:

(i) to compare normalised chloride release rates obtained with known data for other chloride extraction methods;

(ii) see if it made mechanical removal of concretion and redeposited copper in corrosion layers easier;

(iii) to monitor the presence of zinc and tin in solution if suitable material was available.

Experimental Procedure and Materials

Copper sheeting from the wreck of the "Rapid" 1811 and the "Verguilde Draeck" (Gilt Dragon) 1656 were used as obtained ie, barnacles, copper hydroxy chlorides and all. Three low tin low lead wrought copper nails from the "Rapid" which had already been stripped and washed in sesquicarbonate were also treated. One nail out of a set of three aerobically corroded nails (two of which had been previously examined as to composition and chloride release rates in sesquicarbonate) were also treated. The surface area of each item was calculated before treatment.

Solutions were prepared using commercial sodium dithionite, analytical grade sodium hydroxide and distilled deionised water. The preparation was that derived by MacLeod and North (1979) and described in Pearson (1981) for silver reduction. A glass reaction vessel of appropriate volume was used and samples removed for analysis using a hypodermic syringe pushed through a subaseal which sealed the central port.

After the chloride release rate had reached a plateau the copper sheeting was removed and the solutions filtered. The liquor was analysed for dissolved metal species using a Varian absorption spectphotometer and the dried sludge subjected to acid digestion with analytical grade acids and analysed for metal species by AAS.

The first lot of metal sheet (GT3027, GT 3041, RP 2919) was subjected to a further dithionite wash and chloride levels in the solution were monitored.

The surface potential of the copper in the sodium dithionite was obtained for copper sheeting No. I using a platinum electrode at the metal surface and a Ag/AgCl reference electrode in the solution which was calibrated using a quinihydrone solution in a pH 4.0 buffer.

A sample of the treated metal sheet was dissolved in analytical grade 3 M nitric acid plus analytical grade tartaric acid with warming and analysed for chlorides. A core sample of Rapid nail 2918 No. 3 was also taken and similarly prepared for chloride analysis.

Modifications to Experimental Procedure

The preparation for analysis of chlorides was modified during the experiment.

The sample taken when the experiment began was limited to 1 ml in order to reduce volume errors and the solution was subjected to repeated digestion with a 5ml aliquot of 3 Molar sulphuric acid (H_2SO_4) and evaporated until sulphur dioxide fumes were evolved. Erratic chloride readings were obtained.

A larger aliquot (5ml) was then used and heated with 3 M H_2SO_4 until the volume was less than 10ml. The removal of interfering sulphur species was effected by the disproportionation of the sulphur containing ions in solution and/or their oxidation to sulphate ions. The sulphur precipitate was removed by centrifugation.

This technique was chosen because it was found that vacuum filtration using sintered glass crucibles gave low chloride results. Although the chloride could be recovered by acid digestion of the residue on the crucibles the many steps involved substantially increased the experimental error and the time taken to achieve a result.

Variable results were still being obtained and it was not until sulphuric acid was replaced with nitric that consistent results were achieved on multiple samples.

The final procedure adopted was as follows: 8ml of 3 M HNO_3 was added to 5ml aliquot of sample solution which was warmed for several hours on a hot plate until its volume was less than 10ml. The sample was then made up to volume in a 10ml volumetric flask with deionised/distilled water after elemental sulphur had been removed by centifugation. A Buchler Cotlove chloridometer was used to obtain duplicate chloride readings in parts per million (ppm), on the prepared sample.

As can be seen from raw data, consistently useful results were not obtained until the 5th May. After discarding all the results which were obviously incorrect sufficient data remained for plots of chloride concentration (ppm) versus time $^{\frac{1}{2}}$ ($HR^{\frac{1}{2}}$) to be drawn.

The chloride N values; mg per cm^2 per $hr^{\frac{1}{2}}$ were calculated from the slopes obtained. Results are shown in Tables 7 and 8.

Object	Surface Area cm^2	Volume mls	Slope $mg/hr^{\frac{1}{2}}$	N $mg/cm^2/hr^{\frac{1}{2}}$	Total Chloride Released (mg)
Copper Nails RP2918 No 3	67.075	500	14.5 ∓ 8.47	$0.108 \mp .0630$	104.75
Copper Sheet No I GT3027, GT3041, RP2919	340.99	2000	17.01 ∓ 1.28	$0.100 \mp .0075$	354.0
Copper Sheet II GT3027, GT3039	991.26	2400	36.32 ∓ 7.76	$0.093 \mp .019$	649.8

Average N; Release Rate for Chlorides = $0.100 \mp .030\ mg/cm^2/hr^{\frac{1}{2}}$

TABLE 8 - CHLORIDE LEVELS IN TREATED METAL

	Final Concentration of Sample	Chloride Detected (ppm)	% Cl
GT 3039	0.1449g in 100 ml	8.01	0.39
RP Nail 2918 No 3	0.6454g in 100 ml	6.03	0.09

<u>Note</u>: The prefix GT refers to material recovered from the "Verguide Draeck" (1656) and RP prefixes material from the "Rapid" (1811).

Initial Results

The release rate for chlorides was found by experiment to be 0.100 ± .030 $mg/cm^2/hr^{\frac{1}{2}}$. This is larger by a factor of 100 than chloride release rates obtained by normal washing regimes. The surface potential at the end of the experiment was -0.853 mV wrt. N.H.E.

For a mass of 131.33g having a surface area of 340.99 cm^2 recovered from the seabed after 300 years of aerobic corrosion 2000 ml of alkaline dithionite solution for 120 hrs was sufficient to remove chlorides. A repeat treatment gave chloride readings at the lower limits of detection for the experimental method.

The analysis of chlorides in samples of treated metal from GT 3038 and nail No. 3 gave unreliable results given the high concentration of cations such as copper and anions such as nitrate. The latter could not be removed without loss of chloride. A dithionite reduction was attempted to remove cations but the anions remaining in solution interferred with the chloridometer analysis and a repeated analysis is necessary. 0.39% and 0.09% (resp) were the results obtained.

An inspection of the analysis for metal species in spent liquor and sludge suggests that copper, lead and silver in the corrosion layer were successfully reduced and removed in the sludge.

After reduction the objects were washed down with a soft brush under running water. They appeared dark, even after all loose copper was removed, and this may make the treatment inappropriate for certain artifacts.

The barnacles attached to some pieces of sheeting were cleaned up by the treatment as redeposited copper corrosion products were removed from the shells. These shells were easily removed. On some sheets the fine pattern of long gone colonies of marine organisms could be clearly seen after reduction, marked out in reduced copper.

Further Investigations

The effects of dithionite reduction on copper corrosion products was further investigated using 2753.74g of the corroded remains of candlesticks recovered from the "Vergulde Draeck" (1956).

dithionite. Deionised water was used.

The sealed barrel was gently agitated each day and at 498 hrs was reopened. Samples of spent liquor were obtained for metal and chloride analysis and the potential of the solution measured as before. There was a low yield of sludge and this was not retained for analysis. The candlesticks were washed and examined ready for a further dithionite treatment. This was not accomplished during my internship.

Further Results

The potential at the metal surface immediately after opening was -0.872mV wrt N.H.E. 3.824g of chloride was removed from the candlesticks during this first dithionite treatment while only trace amounts of copper and zinc were detected in the liquor. 315mg of tin was removed in the liquor.

Discussion

At the time of writing the investigations were incomplete. Besides the brass candlesticks six lots of 3rd century BC coins from an egyptian site were being treated.

These had been previously treated circa (1970) with a citric acid deconcretion followed by a protective treatment in benzotriazole and lacquering with "Incralac". The metal in these objects was very porous and much of the total substance of the artifacts had corroded away. Localised pale grey-green mounds of copper chlorides were present indicating that accelerated copper corrosion was occurring.

<u>Method</u>: Prior to immersion in alkaline dithionite the brass candlesticks were washed in an acetone bath to remove Incralac. They were then placed in 0.2m potassium nitrate solution so that a chloride release rate could be plotted and compared with the release rate obtained in alkaline dithionite solution.

The chlorides measured in this initial wash were not linear with respect to hours $^{\frac{1}{2}}$ and were accompanied into solution by zinc and lead ions. At 143 hrs 10g.litre of hexamine was added to the wash and the release of all species monitored was reduced markedly.

At 210 hrs the brass was placed in a 25 litre 1 black plastic barrel with a tight sealing screw lid. The barrel was filled with alkaline dithionite solution made up with a commercial caustic soda (NaOH), as a 1 Molar solution containing 5% by weight of commercial sodium

These had already had several dithionite treatments and were still releasing chloride at the same high rate. The rate of release appeared to be independent of the total chloride contained in the corrosion.

The rapid loss of zinc from the corroded brass candlesticks during their pre- reduction wash in 0.2m KNO_3, highlights the need to monitor wash solutions and to plot the data obtained as slopes of concentration versus time$^{\frac{1}{2}}$.

The lack of linearity in this plot indicated that it was not a diffusion controlled process and corrosion was occurring.

The surface potentials obtained confirmed that no undue ingress of air causing oxidation of the dithionite had occurred and that the effective redox potential of the solution remained sufficiently high to reduce copper species present.

Conclusion

The use of alkaline sodium dithionite solutions for treatment of corroded copper artifacts appears promising. Chloride release rates are 100 times greater than usual aqueous washing regimes.

The usual patination found on copper and bronze is reduced to finely divided metal and falls or can be brushed off the object. Small details on the surfaces of the artifact are retained if the corrosion has been uniform and errosion has not occurred.

The residual sulphate remaining in the micro pores after reduction and washing can produce copper sulphate containing patina's on exposure to air. The difficulties encountered in safely removing sulphate ions makes dithionite and sulphate reduction a limited treatment for iron objects. However, unlike iron copper is not adversely affected by a low concentration of sulphate ions.

Thus, the treatment should be considered in those cases where the more familiar electrolytic reduction or electrolysis are indicated.

The possibility of using dithionite in a poultice on localised outbreaker of "bronze disease" should also be investigated as the dark surface formed after reduction will blend well with intact patina.

<u>Attachments</u>: Illustration 13 - Copper Sheeting Before
Dithionite Treatment

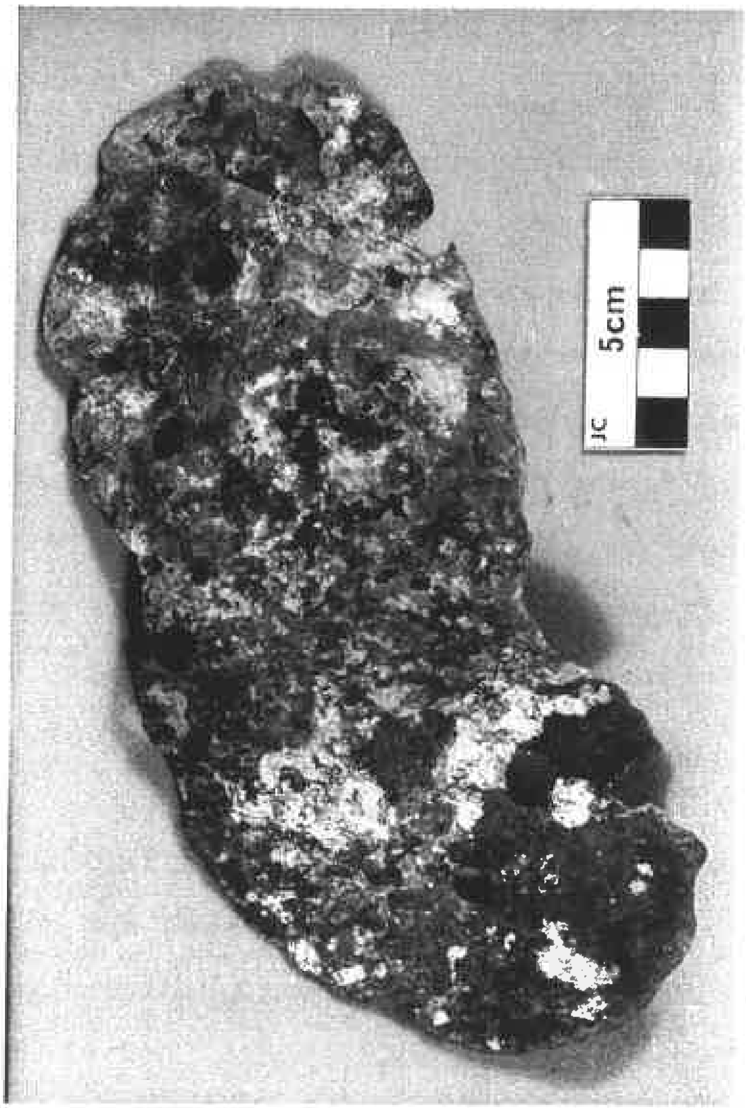


Illustration No 13.

G.T. 3038 before Dithionite treatment.

CONSERVATION FACILITIES AT THE W.A. MUSEUM

General Description

The Conservation section at the W.A. Museum is housed in Freemantle 30 km away from its administrative centre at Francis St, Perth. It is part of the Museum's Department of Professional Services. See Illustration 14.

The Conservation section consists of new facilities at Cliff St which became operational in October 1980 and the previous conservation centre a converted shed at Finnerty St, Freemantle. This is now used as an open work area for restoration of vehicles and other larger objects as well as housing the P.E.G. impregnation tanks, hot wax baths and outside, electrolysis tanks for cannon.

The Cliff St building was originally a Government store which has been tastefully converted to its new purpose by retaining the original door fittings, restoring Jarrah block floors and limestone walls. Ceilings are generally absent and most of each section of the building is divided into areas by partitioning thereby retaining the open beam roof.

The conservation areas includes a large chemistry laboratory, a restoration area, a textile area, a ground floor wet work area, offices, a dark room and staff facilities. Small rooms have been set aside for special tasks, and include a room for plastic replication work and dirty or noisy restoration tasks such as Vibrotool or drilling operations. This room is equipped with a fume cupboard and a source of natural light. Textiles has a clean room for delicate tasks and their transmitted light microscope is housed here. It also has a fume cupboard. An instrument room, fully enclosed with no windows houses the ultra violet/visible spectrophotometer and potentiostat equipment.

The wet area on the ground floor opens into a courtyard and small rooms at the rear of this yard house chemical stores and a workshop which at present is used for section polishing.

The Cliff St building also houses the maritime archaeology section of the museum as well as the yet unfinished maritime museum exhibition areas. Thus carpentary /metal workshops and office services are shared by all sections.

As exhibitions, maritime archaeology and conservation are at various times involved with larger artifacts and equipment provision has been made for vehicle (including fork lift) access to all ground floor facilities. A lift is provided between floors with access by wide corridors to wet areas and outside.

Conservation Section

a. Functions and Organisation

The overall design of the laboratories and their equipages reflect the special interests of the W.A. Museum and they are are therefore not representative of conservation laboratories elsewhere in Australia. 60% of objects treated originate with maritime archaeology and these generally require conservation rather than restoration. Many objects treated are unlikely to be displayed being multiples of fragments of structural elements and artifacts from various wreck sites.

Their conservation is chemistry orientated, the treatments employed are best described as chemical engineering processes developed for the various material classifications encountered. 30% of objects treated are from the History section of the Museum. Such objects include vehicles, textiles, ethnographic material and everyday paraphenalia usually from the Australian Colonial period.

The rest of the work of the conservation section is split between the other sections of the museum such as Anthropology, Aboriginal sites, Natural Sciences, Branch Museums and Outstations and includes work and advice for affiliated country museums, members of the public, and Government organisations.

There are seventeen staff employed in the Conservation Section. Not all these are full-time.

The overall running of the section is the concern of the Head Conservator. Two curators of conservation each manage a sub section:

(i) Chemistry and Conservation
(ii) Textiles and Restoration

A research officer is also employed.

Many of the conservation staff are experienced divers and need to be if in situ measurements of pH and potential are to be made at wreck sites. A knowledge of or ability to learn diving techniques can be considered a prerequisite for employment as a maritime archaeology conservator.

b. Laboratory Equipment.

Equipment peculiar to the conservation function of the laboratory include:

(i) A hydrogen reduction furnace. This has been described in the paper by North and Owens (1981) and a copy of its diagramatic representation is included. Illustration 16 as well as notes on its operation prepared by M. Owens, Annex 4 -

(ii) De-Humidification chambers for the Batavian timbers. A layout of the shed which houses the dehumidification chambers is attached in Annex 4.

Not shown on the diagram is the roller doors to the South shed which have been sealed inside with a removable section of insulated wall. This allows the positioning of large timbers in the chamber and their removal to the Batavia gallery after treatment.

The sheds have their own air conditioning system and have been lined with fibro and insulated. Temperatures of 5-35^{O}C can be maintained with a humidity of 10-100%.

(iii) A modified washing machine for the desalination of ceramics.

(iv) Potentiostat, X Y recorder and programmer. This equipment is used in the study of corrosion processes and is an essential research tool for investigations undertaken by the W.A. Museum conservation section.

(v) Absorption Spectrophotometer (Varian AA4). This machine was purchased second hand and is used for monitoring metal species during washing procedures and for compositional analysis of metal alloys and corrosion products.

(vi) Chlordometer (Buchler Cotlove)
The quick analysis as chloride levels is essential for monitoring the removal of chlorides from most materials treated in the laboratory. It is much quicker to standardise than a specific ion electrode and more durable. Only 1ml of a solution is required to obtain reproducible results of less than 1ppm.

(vii) A freeze drier developed and built by J. Pang (1982) for treating waterlogged organic materials. See Illustration 15.

As mentioned previously polyethyleneglycol impregnation tanks, wax impregnation tanks and electrolysis tanks are housed at Finnerty St.

Design Features in the Laboratory

(i) The laboratory on all floors is equipped with piped deionised water obtained from an automatic deioniser on the ground floor. The water cuts out when the conductivity rises above a pre-set level. Recharging is a matter of turning taps which allow acid and alkali stored in tanks outside to flow through the appropriate resin column and be discharged.

(ii) Hydrogen and nitrogen gas are piped to various points in the laboratory. Air outlets are also provided. The AA is connected to air, acetylene and nitrous oxide. All gases are housed outside the laboratory in a screened off area adjacent to the delivery gate in the back courtyard.

(iii) Fume hoods; a total of five separate systems have been provided throughout the laboratory. Two are provided in chemistry. The large one is lined with stainless steel 316 and is solvent resistent. The other intended for treatments using oxidising acids was designed for radio chemistry and has a wash system at the back. The restoration area is equipped with a clear sided glove box over a shallow stainless steel bath connected to water taps as well as a clear fume hood enclosing a work area. This is used for tasks where noxious fumes can be a problem, eg consolidation treatments for woods or ceramics.

The remaining two fume cupboards are located in textiles and the plastics room.

One bench in chemistry is connected to a directed airflow system. Adjustable vents at the back of the bench allow unpleasant or harmful fumes to be removed from the local work area.

(iv) All bench tops have been coated with a solvent and acid resistant clear coating. The floor is covered with vinyl tiles and drainage points have been provided.

Safety

Safety regulations are strictly adhered to in the chemistry laboratory. Face shields, safety glasses, rubber gloves and earmuffs are readily available. Appropriate clothing must be worn and open work shoes are forbidden. Eyewash bottles are provided at each bench and a first aid box is centrally located and clearly marked.

A complete breathing apparatus connected to a bottle of medical air is visible in the laboratory and five extinguishers (foam and BCF) are within easy reach of each bench.

A fire alarm system is connected directly to the fire station and when activated cuttsoff all the exhaust systems and the air conditioning. No sprinklers are provided as it is believed that these can cause more damage than good.

Deadly substances such as cyanide preparations are stored in a locked glass fronted cupboard. All chemicals are clearly labelled and only a minimum of bulk solvents are shelved. Stock solvents are stored in a flammable store at the rear of the courtyard on wooden shelving. Sufficient pumps are available for transferring these liquids without spillage into containers. Carrying baskets are provided for safe handling.

Now that the maritime archaeology section has opened there are two stairways which can be used to exit from the top floor. However, both of these are wooden and there is no system of fire retardant doors between one section and another.

Windows are barred in keeping with the original appearance of a bond store and in my opinion escape routes from any serious conflagration during working hours are inadequate.

Documentation

The procedure followed at the W.A. Museum is the same as that instituted during the time Dr C. Pearson was the head of its Conservation Section. (Samples of the forms and envelope enclosures are included in the relevant annex). Recently, the Restoration and Textiles Section has adopted the format devised by the C.C.A.E. (A sample of this type of Report is also annexed). Maintenance and treatment of Vehicles and other large items are generally documented on the relevant Museum file for each such object and when I left W.A. a system for ensuring regular maintenance occurred for vehicles was being set up.

Staff Development and Education Programmes

Training programmes for technical staff were in operation and included lectures by staff members on the various functions of the Museum. (A programme is annexed.) The conservation section runs regular training programmes for members of country museums and is/was involved in the W.A.I.T. course in marine archaeology.

Future Developments

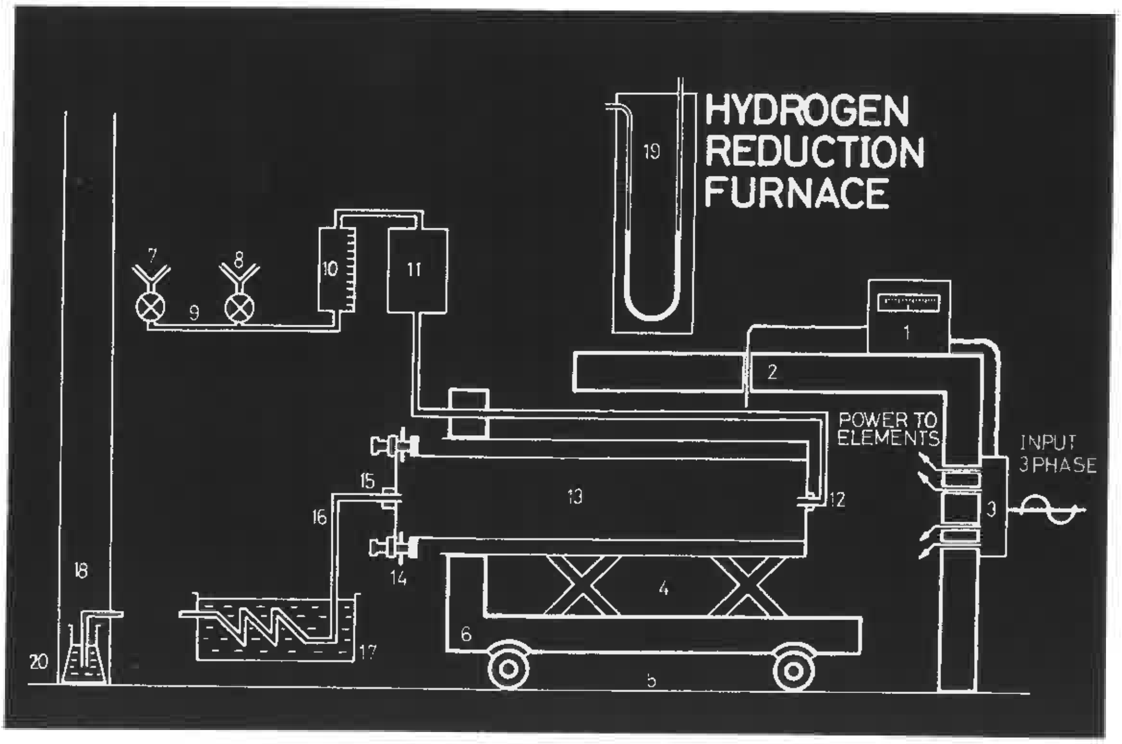
The Conservation section while retaining its well founded reputation as a centre for research and treatment of objects recovered from the sea could given the opportunity expand its activities in the conservation and restoration of historical artifacts and ethnographic materials.

The accreditation system for small museums in operation in W.A. is very successful and has led to a lively interest in museums and history throughout the state. However, the sections manpower resources are severely strained maintaining contact and servicing these museums, given the long distances that need to be travelled and thus time away from the laboratory for the conservator involved.

As is so often the case an obvious requirement (a travelling conservator) must wait until finances can be made available.

Illus. 14. The W.A Maritime Museum.

Illus. 15. The Freeze Drier built by
Dr. James Pang.



Illus. 16. from North and Owens 1981.

REFERENCES

CAMPBELL, H.S., MILLS D.J., (1976)

"A Metallurgical Study of Objects Salvaged from the Sea". Report CD1 for Metal User's Consultancy Service. BNF Metals Technology Centre; Oxfordshire.

*
MACLEOD, I.D. (1982)

"Formation of Marine Concretions on Copper and its Alloys: - Int J. Naut Archy 11(3)

MACLEOD, I.D., NORTH W.A. (1982)

"Conservation of a Composite Cannon - 'Batavia' - 1629"
Int J. Naut. Arch. 11(3)

MACLEOD, I.D. (1981)

"Bronze Disease - an Electrochemical Explanation"
ICCM Bulletin VII(1) pp 16-26

MERK, L.A. (1978)

"A Study of Reagents Used in the Stripping of Bronzes"
Studies in Conservation, Vol. 23 pp 15-22

NORTH, W.A., PEARSON, C. (1978)

"Washing Methods for Cl - Removal from Marine Iron"
Studies in Conservation Vol. 23 pp 174-186

NORTH, W.A., OWENS, M. (1981)

"Design and Operation of a H_2 Furnace for Treatment of Marine Iron"
Int J. Naut. Arch. 10 pp 95-100

PANG, J.T. (1981)

"The Treatment of Waterlogged Oak Timbers from a 17th Century Dutch East Indian, 'Batavia', using Polyethylene glycol - Preprints"
ICCOM 6th Trennial Meeting - Ottawa 8/7/6

PANG, J.T. (1982)

"The Design of a Freeze-drying system used in the Conservation of Waterlogged Materials" : International Journal of Nautical Archaeology and Underwater Exploration; Vol 11., No. 2., pp 105-111

* MACLEOD I.D; NORTH W.A.; (1979)

Conservation of Corroded Silver Studies in Cons. Vol 24 pg 165-170

PEARSON, C. (1981)

"Conservation of the Underwater Heritage" in
Protection of the Underwater Heritage
Technical Handbooks for Museums and Monuments No. 4

ROBINSON, B.W. (1980)

"The Backscattered Electron/Low Vacuum SEM Technique :
A Users Evaluation." MICRON Vol. II., pp 333-334

WEISSER, T.S. (1975)

"The De-Alloying of Copper Alloys" Conservation in Archeology
pp 207 - 214 and the Applied Arts I.I.C. Lond

BROWN B.F. etal, (1977)

"Corrosion and Metal Artifacts" N.B.S.S publication 479

U.S.A pp 252.

ANNEX 1 - GUIDELINES FOR INTERNSHIP REPORT

GUIDELINES FOR INTERNSHIP REQUIREMENTS OF MASTER OF APPLIED SCIENCE IN MATERIALS CONSERVATION

nternship Requirements

he Higher Degree Committee of the College has approved the following equirements for the Internship of the Master of Applied Science in Materials onservation.

1. The internship will be for a period of at least six months.
2. The internship will be carried out under the supervision of a conservator at an accredited institution (as approved by the Higher Degree Committee) in the student's field of interest.
3. Following completion of the internship the student will be required to provide a dissertation of the work carried out, including case studies.
4. The dissertation and candidate will be examined by a panel. This panel will consist of the Materials Conservation Course Coordinator, the lecturer responsible for the area of specialisation in which the internship is carried out, and at least one external examiner. This panel will report to the Higher Degree Committee.
   Where it is difficult for a student to be examined in Australia, e.g. an overseas student carrying out the internship in their own country, an overseas panel of relevant experts will be selected to examine the student and report on the oral examination. A copy of the dissertation, and the report of this panel will be submitted to the Higher Degree Committee.
   Either panel will be approved by the Higher Degree Committee. The panel will take into account the report(s) from the Head Conservator(s) of the institution(s) accepting the intern, on the ability of the intern and the conservation work carried out.

ms and Objectives

e aims and objectives of the internship are to further the student's aining in their field of specialisation. This is best achieved by studying a 1:1 basis with an experienced qualified conservator, where the theory d practice acquired in the College lecture room and laboratory can be vanced, but under direction and close supervision. It is expected that e intern will not just observe, but also assist the conservator with advanced nservation treatments of works of art and artefacts. In addition, the tern will carry out treatment of other works on an individual basis.

ypical programme of work in a specialised area of conservation will include:

1. Learn and execute with proficiency all the basic conservation and restoration techniques.
2. Learn and execute more advanced techniques under the direction of the conservator.

.../2.

3. Duplicating must be by a method giving a clear and permanent copy (e.g. Multilith, Xerox or Stencil Duplicating). Use of spirit duplicators is not acceptable.

4. One side of the sheet only may be used, with the following minimal margins:

left-hand margin	4 cm
right-hand margin	2 cm
top and lower margins	2 cm

5. Pages must be numbered consecutively throughout the dissertation.

6. Sheets of B4 size shall be folded and bound so as to open at the top and the right.

7. Where the written dissertation is accompanied by supplementary non-print material, such as photographs, this will need to be reproduced in a form suitable for storage and retrieval purposes.

Presentation

1. One bound copy of the dissertation and the unbound original must be submitted to the Academic Registrar, and must be accompanied by a statement by the candidate certifying to the original authorship of the dissertation.

2. The first page should identify the work as a dissertation submitted for the Degree of Master of the Canberra College of Advanced Education, the candidate's name, the full title of the dissertation and the month and year of submission.

3. The next page should contain a summary of the work, usually in the order of 250 words.

4. There should be a table of contents at the beginning of the work and, at the end, a list of references used.

5. There should be, in the prefactory comments, an acknowledgement of assistance and advice received.

6. Advice on bibliographical standards may be given by the Supervisor or the School responsible for the programme of study. It is essential that dissertations reflect accurate and consistent acknowledgement of sources.

7. Academic Board seeks simplicity and directness of writing style, and expects a high standard of editing to be evident in work submitted for examination.

8. Binding of dissertations, other than the original, is the responsibility of the candidate. Binding of the original will be undertaken only after Academic Board has indicated that a particular candidate has satisfied all of the requirements of the particular Master's programme, and will be the responsibility of the College Library.

..../4.

CORROSION LAYER - ANALYSIS - VALUES EXPRESSED AS PERCENTAGES

Nail	Cu	Sn	Pb	Zn	Sb	Ca	Mg	Ag	Cl
A/5									
B/2b	71.3	N/D	0.18	0.0019	0.0102	0.01	0.01	.0021	1.37
C/2a	33.5	N/D	0.22	0.0072	0.0089	0.82	0.57	.0149	1.68
D/1b	55.0	N/D	0.02	0.0018	0.0101	0.02	0.03	0.00098	2.15
E/3	40.8	N/D	0.02	0.0013	0.0060	0.56	0.03	0.0060	3.11
F/1a	43.14	N/D	0.38	0.0072	0.0438	0.33	0.14	0.0049	3.42
G/4	-	N/A							
C/2 aer	-	N/A							

N/D Not Detected

N/A Not Applicable (No Corrosion Layer Retained)

RAW DATA/METAL ANALYSIS (PPM)

Vol = 50ml

Nail	Cu	Sn	Pb	Zn	Sb	Ni	Ag	Cl
A/[illegible] wt (mg) 60.7	426.4	/D	1.64	.06	1.27	.006	-	-
B/2b 76.9	1044.9	"	2.15	.09	0.95	.001		
C/2a 24.8	445.6		0.89	.08	0.79	.0015		
D/1b 116.0	2228.1	4.4	0.25	0.12	0.63	.006		
E/3 48.9	925.8	3.4	0.13	0.10	0.63	.004		
F/1a 183.5	2996.5	2.9	8.48	0.18	1.90	.016		
G/4 75.1	1383.0	3.4	0.38	0.07	0.79			
C/$_{2}^{aer}$ 28.5	399.5	46.2	5.95	1.56	1.11	.004		

ME 5223 Anaerobic : Alk. Rochelle treated A/5

5.

ainer A Final wt. 619.23g

me 1000

	l	26.15 m
	wt	641.68g
	av diam	2.09cm
	S/Area	188.7cm^2

ription: Dark friable patina
striations visible

hrs$^{\frac{1}{2}}$)	t Hrs.	Date	Time	Cu ppm	Cl ppm	1st Wash 1000ml	
	0	15/2	1.00pm				
	1		2.00pm	1)	1		
	2.75		3.45pm	1.9)	0.5		
	19	16/2	9.00	2.03)	-		
	25		4.00	4.82)	2.03		
	67	18/2	9.00	-)		pH	
	91	19/2		4.4)	-		
	125	22/2		5)	-	10.20	
	174	24/2		3.5)	1.8	10.13	
	222	26/2		4.3)	0.2	10.32	
	320	2/3		1.5)	0.2	10.69	
	367	4/3		)	1.6	-	
						2nd Wash (1000m	
	24	5/3		0.4)	1.6)	1.1*)	
	96	8/3		1.9)	8.1)	5.8*)	
	144	10/3		2.8)	17.4 }	12.4*)	
	192	12/3		3.7)	18.7	13.2*)	Zn ppm
	264	15/3		5.5)	17.9		
	264	15/3*		-)	12.3 *		0.24
	312	17/3		5.95)	12.8		-
	360	19/3		6.6)	12.3		
	432	22/3		7.4)	13.5		
	600	29/3		11.4)	13.2		
	654	31/3	3.00	)		Combined Wash (ACE) S/A = 371.84 cm^2	
	697	2/4		-)	-		
	769	5/4		2.2)	14.3?		
	816.9	7/4		3.5)	11.6)		
	978.9	14/4		5.0)	14.2)		
	111.9	23/4		6.8)	19.1)		
	1367	30/4		8.9)	22.9)		
	1775	17/5		9.1)	23.9 - ppte of blue		
	2157	2/6		)	17.3 green material		
				3rd wash (ACE)			

sh
slp = 0.20 ∓ .08
N = 1.07 ∓ 10^{-3}
106

Cl$_{(4)}$ slp = 1.36 ∓ 0.11
N = 3.66 x 10^{-3}

sh
slp = 1.43 ∓ 0.25 (corrected data*)
N = 7.6 x 10^{-3}

Cu$_{(6)}$ slp = 0.49 ∓ 0.08
N = 1.32 x 10^{-3}

slp = 2.01 ∓ .36 (raw data)
N = 10.8 x 10^{-3}

slp = 0.54 ∓ .05
N = 2.9 x 10-3

ANNEX 2. CHLORIDE LEVELS AND RELEASE RATES DURING THE WASHING OF COPPER NAILS FROM THE RAPID

Nail	Cu	Sn	Pb	Zn	Sb	Ca	Mg	Ag	Cl
A/5									
B/2b	71.3	N/D	0.18	0.0019	0.0102	0.01	0.01	.0021	1.37
C/2a	33.5	N/D	0.22	0.0072	0.0089	0.82	0.57	.0149	1.68
D/1b	55.0	N/D	0.02	0.0018	0.0101	0.02	0.03	0.00098	2.15
E/3	40.8	N/D	0.02	0.0013	0.0060	0.56	0.03	0.0060	3.11
F/1a	43.14	N/D	0.38	0.0072	0.0438	0.33	0.14	0.0049	3.42
G/4	-	N/A							
C/2 aer	-	N/A							

N/D Not Detected

N/A Not Applicable (No Corrosion Layer Retained)

RAW DATA/METAL ANALYSIS (PPM)

Vol = 50ml

Nail	Cu	Sn	Pb	Zn	Sb	Ni	Ag	Cl
A/ wt (mg) 60.7	426.4	/D	1.64	.06	1.27	.006	-	-
B/2b 76.9	1044.9	"	2.15	.09	0.95	.001		
C/2a 24.8	445.6		0.89	.08	0.79	.0015		
D/1b 116.0	2228.1	4.4	0.25	0.12	0.63	.006		
E/3 48.9	925.8	3.4	0.13	0.10	0.63	.004		
F/1a 183.5	2996.5	2.9	8.48	0.18	1.90	.016		
G/4 75.1	1383.0	3.4	0.38	0.07	0.79			
$C/_{2}^{aer}$ 28.5	399.5	46.2	5.95	1.56	1.11	.004		

Descr: dark friable material over dark patina/generally smooth appearance/ some striations.

wt = 282.24g
av diam = 1.95cm
S/Area = 79.46 sq.cm^2

Final wt: 279.01 g

$t_{\frac{1}{2}}$		Date	time	t hrs		Cu ppm	Cl ppm	pH	600ml 1st Wash
	0	15/2	1.00pm		0	-	-	Zn	
	1	15/2	2.00pm		1	.01	-	0.23	
	1.56	15/2	3.45pm		2.45	.11	0.4		
	4.3	16/2	9.00am		19	.13	0.5		
	5	16/2	4.00pm		25	.24	-		Wash soln. contaminated; pH 13.95
	8.18	18/2	9.00am		67	-	1.0		
	9.54	19/2	9.00am		91	.60	-		
	11.2	22/2	9.00am		125	1.30	1.1		
	13.2	24/2	9.00am		174	.60	1.2	9.62	
	14.9	26/2	9.00am		222	1.10	-	10.09	
	17.9	2/3	9.00am		320	.80	0.2	9.87	
	19.2	4/3	9.00am		367	-	-	10.20	
4.8	19.7	5/3	9.00am	24	391	1.7	6.05		600ml 2nd Wash New soln. 1% sesquicarb. pH 10.05
9.7	21.5	8/3	9.00am	96	463	1.4	10.1		
12.	22.6	10/3	9.00am	144	511	2.4	19.0		
13.8	23.6	12/3	9.00am	192		3.4	20.3	Zn	
16.2	25.1	15/3	9.00am	264	631	5.8	18.1	0.88	
11.11	*		*				17.3*	-	
17.7	26.0	17/3	9.00am	312	678	5.6	14.5	0.92	
19.0	26.9	19/3	9.00am	360	727	7.3	17.3	-	
20.8	28.2	22/3	9.00am	432	799	9.0	12.7	1.09 =	.62mg
24.5	31.0	29/3	9.00am	600	967	11.2	17.8	-	
26.4		2/4	10.00am	654		-	-		1000ml 3rd Wash pH 9.82 1% sesquicarb.
26.9		5/4		726		0.85	0.6		
28.2		7/4		798		1.56	1.8		
30.7		14/4		942		3.45	1.3		
34.0		23/4		1156		3.75	3.0		
36.4		30/4		1324		4.58	1.8		

Normalized Data -	Cl^-	Cu	Slopes:	Cl	Cu
1st wash	0.5	0.5		0.07 ∓ .01	0.06 ∓ 0.02
2nd wash	12.2	5.1		1.61 ∓ 0.38	0.69 ∓ 0.04
3rd wash	3.5	4.8		0.28 ∓ 0.12	0.38 ∓ 0.07

Nail: 2a

Container: C

1 = 11.44cm
wt = 213.14g
av diam = 1.73cm
S/Area = 66.90cm^2

wt loss on acid treatment: -5.49g

Final wt: 207.48 (ie + .03g)

Descr: Dark friable material over dark patina/some tenacious concretions overlying deep pitting/waisted shape with obvious striation

$t_{\frac{1}{2}}$		Date	time	t (Hrs)		Cu (ppm)	Cl (ppm)		pH		600ml 1st Wash
	0	15/2	1.00pm		0	-	-			Zn 0.3	(ppm)
	1	15/2	2.00pm		1	-	-				
	1.56	15/2	3.45pm		2.45	.11	0				
	4.3	16/2	9.00am		19	.11	0.4				
	5	16/2	4.00pm		25	.13	-				Wash soln.
	8.18	18/2	9.00am		67	.30	2.6				contaminated;
	9.54	19/2	9.00am		91	.14	1.4				pH 13.95
	11.2	22/2	9.00am		125	.6	3.8		9.72		
	13.2	24/2	9.00am		174	.6	3.3		9.80		
	14.9	26/2	9.00am		222	.9	4.0		9.72		
	17.9	2/3	9.00am		320	.4	2.1		10.81		
	19.2	4/3	9.00am		367	-	-		-		
4.8	19.7	5/3	9.00am	24	391	0.4	4.74				500ml 2nd Wash
9.7	21.5	8/3	9.00am	96	463	0.8	27.1	8.35			New soln.
12.	22.6	10/3	9.00am	144	511	1.2	13.8				1% sesquicarb.
13.8	23.6	12/3	9.00am	192		2.4	14.2				pH 10.05
16.2	25.1	15/3	9.00am	264	631	4.3	12.5			Zn 0.6	
11.11	*		*				11.9*			-	
17.7	26.0	17/3	9.00am	312	678	5.0	11.6			0.6	
19.0	26.9	19/3	9.00am	360	727	5.8	11.9			-	
20.8	28.2	22/3	9.00am	432	799	7.8	16.9			0.6	
24.5	31.0	29/3	9.00am	600	967	11.6	12.2			-	Combined Wash
26.4		2/4	10.00am	654							container "A"
26.9		5/4		726							1000ml 3rd Wash
28.2		7/4		798							pH 9.82
30.7		14/4		942							1% sesquicarb.
34.0		23/4		1156							
36.4		30/4		1324							

Normalized Data - x 10^{-3}	Cl^-	Cu	Slopes:	Cl	Cu
1st wash	-	-		-	-
2nd wash	8.4	6.54		1.13 ∓ 0.22	0.73 ∓ 0.06
3rd wash ACE combined, wash see sheet "A"					

Descr: Dk friable patina over dk surfaces/ wrought pattern visible/pointed/ some tenacious concretions/no deep pitting

av diam = 1.67cm
S/Area = 79.75cm^2

Final wt: 280.5g

t½	Hrs	Date	time	t	Hrs	Cl ppm	Cl ppm	pH	600ml 1st Wash
	0	15/2	1.00pm		0			Zn 0.4	(ppm)
	1	15/2	2.00pm		1				
	1.56	15/2	3.45pm		2.45				
	4.3	16/2	9.00am		19				
	5	16/2	4.00pm		25				Wash soln. contaminated; pH 13.95
	8.18	18/2	9.00am		67				
	9.54	19/2	9.00am		91				
	11.2	22/2	9.00am		125				
	13.2	24/2	9.00am		174				
	14.9	26/2	9.00am		222				
	17.9	2/3	9.00am		320				
	19.2	4/3	9.00am		367				
4.8	19.7	5/3	9.00am	24	391				600ml 2nd Wash New soln. 1% sesquicarb. pH 10.05
9.7	21.5	8/3	9.00am	96	463				
12.	22.6	10/3	9.00am	144	511				
13.8	23.6	12/3	9.00am	192					
16.2	25.1	15/3	9.00am	264	631			Zn 0.6	(ppm)
11.14	*		*						
17.7	26.0	17/3	9.00am	312	678			0.6	
19.0	26.9	19/3	9.00am	360	727				
20.8	28.2	22/3	9.00am	432	799			0.7	
24.5	31.0	29/3	9.00am	600	967				
26.4		2/4	10.00am	654					
26.9		5/4		726					1000ml 3rd Wash pH 9.82 1% sesquicarb.
28.2		7/4		798					
30.7		14/4		942					
34.0		23/4		1156					
36.4		30/4		1324					

Normalized Data -	Cl$^-$	Cu
1st wash		
2nd wash	11.50	4.50
3rd wash	-	5.38

Slopes:	Cl	Cu
	1.84 ± 0.16	0.45 ± 0.05

<u>Descr</u>: Heavy dark encrustation incorporating small calcareous remains overlying deeply pitted areas. Streations visible on rest of surface which was smooth and shiney and only lightly patinated.

av diam = 1.86cm
S/Area = 118.74cm^2

<u>Final wt:</u> 463.24g

$t_{\frac{1}{2}}$		Date	time	t Hrs		Cu ppm	Clppm	pH	1000ml 1st Wash
0		15/2	1.00pm	0		-	-	Zn 0.35	(ppm) 1% sesquicarbonate
1		15/2	2.00pm	1		0.2	0.6		
1.56		15/2	3.45pm	2.45		0.2	1.0		
4.3		16/2	9.00am	19		0.2	-		
5		16/2	4.00pm	25		0.3	1.3		Wash soln.
8.18		18/2	9.00am	67		-	1.5		contaminated;
9.54		19/2	9.00am	91		0.7	-		pH 13.95
11.2		22/2	9.00am	125		0.9	2.1	9.56	
13.2		24/2	9.00am	174		0.8	2.2	10.20	
14.9		26/2	9.00am	222		0.9	-	9.82	
17.9		2/3	9.00am	320		0.4	-	10.78	
19.2		4/3	9.00am	367		-	2.1	-	
4.8	19.7	5/3	9.00am	24	391	0.7	2.07		1000ml 2nd Wash
9.7	21.5	8/3	9.00am	96	463	1.4	11.00		New soln.
12.	22.6	10/3	9.00am	144	511	2.5	14.8		1% sesquicarb.
13.8	23.6	12/3	9.00am	192		3.0	15.7	Zn	(ppm) pH 10.05
16.2	25.1	15/3	9.00am	264	631	5.2	14.3	0.6	
11.11	*		*				13.1*	-	
17.7	26.0	17/3	9.00am	312	678	5.2	17.7*	0.58	
19.0	26.9	19/3	9.00am	360	727	5.8	19.0*	-	
20.8	28.2	22/3	9.00am	432	799	7.8	20.8*	0.67	
24.5	31.0	29/3	9.00am	600	967	9.3	24.5*	-	Combined wash ACE
26.4		2/4	10.00am	654					
26.9		5/4		726					1000ml 3rd Wash
28.2		7/4		798					pH 9.82
30.7		14/4		942					1% sesquicarb.
34.0		23/4		1156					
36.4		30/4		1324					

Normalized Data -	Cl^-	Cu	Slopes:	Cl	Cl
1st wash	1.0			$0.12 \mp .01$	$0.03 + 0.02$
2nd wash	12.1	3.9		$1.44 \mp .15$	$0.47 \mp .04$
3rd wash					

Descr: Dark patina/large pits. S/Area = 60.55 cm

$t^{\frac{1}{2}}$		Date	time	t Hrs		Cu ppm	Cl ppm	pH	1st Wash 1% sesquicarbonate solution
0		15/2	1.00pm	0		0	0		
1		15/2	2.00pm	1		0.14	1		
1.56		15/2	3.45pm	2.45		0.14	-		
4.3		16/2	9.00am	19		0.20	-		
5		16/2	4.00pm	25		0.32	-		
8.18		18/2	9.00am	67		-	0.6		Wash soln. contaminated; pH 13.95
9.54		19/2	9.00am	91		0.9	-		
11.2		22/2	9.00am	125		1.0	0.4	9.55	
13.2		24/2	9.00am	174		0.5	0.6	10.49	
14.9		26/2	9.00am	222		0.6	-0	10.10	
17.9		2/3	9.00am	320		0.4	-0	11.92	2nd Wash New solution 1% sesquicarbonate; pH 10.05
19.2		4/3	9.00am	367		0.8	-0		
4.8	19.7	5/3	9.00am	24	391	0.2	0.82		
9.7	21.5	8/3	9.00am	96	463	1.2	5.1		
12	22.6	10/3	9.00am	144	511	2.3	15.1		
13.8	23.6	12/3	9.00am	192		2.5	15.2		Zn ppm
16.2	25.1	15/3	9.00am	264	631	4.5	14.4		0.7
16.2	- *		*				12.4*		
17.7	26.0	17/3	9.00am	312	678	4.4	12.6		0.7
19.0	26.9	19/3	9.00am	360	727	4.9	12.4		
20.8	28.2	22/3	9.00am	432	799	6.0	11.5		0.7 1000ml 3rd Wash; pH 9.82 1% sesquicarbonate
24.5	31.0	29/3	9.00am	600	967	7.38	15.36		
26.4		31/3 2/4	10.00am	654		-	-		
26.9		5/4	10.00am	726		0.7	0.0		
28.2		7/4	10.00am	798		0.1	0.3		
30.7		14/4	10.00am	942		2.0	0.7		
34.0		23/4	10.00am	1156		2.3	0.3		
36.4		30/4	10.00am	1324		2.3	0.0		

Normalized Data:-	Cl^-	Cu	Slopes:-	Cl	Cu
1st Wash	-	-		0.06 ∓ 0.2	0.06
2nd Wash	17.28 x 10^{-3}	3.76 x 10^{-3}		1.74 ∓ .46	0.38 ∓ 0.03
3rd Wash		2.87 x 10^{-3}		0.18*	0.29 + 0.12

(3 *points only)

s ME 2918 - Aerobic corrosion (E/1)

l 16.3 5cm Container E (1000ml)
wt 150.72g
am 1.2 26cm
ea $65.33cm^2$

ription - glossy pale green; slightly offset head

	t Hrs	Date	time	Cu ppm	Cl ppm	Pb ppm 1st Wash (1% sesquicarbonate)
	0	21/4	11.15			Slope = 0.58
)5	49.75	23/4	1.00	8.3	7.9	$\pm$ .21
'5	217.75	30/4	1.00	20.7	11.9	N = 8.9×10^{-3}
38	337.75	5/5	1.00	25.5	10.8	
54	385.75	7/5	1.00	34.8	11.6	
39	457.75	10/5	1.00	35.5	12.9	
)1	625.75	17/5	1.00	38.8	21.0,	
	649.75	18/5				
					2nd Wash - (KNO_3 0.2M) 500ml	
19	" "	25/5	10.15	0	0	.009
)0	672.50	26/5	9.00	.04	0.7	.009
15	792.5	31/5	9.00		16.07	Slope = 7.01
	864.5	3/6	9.00		27.16	$\pm$ 0.50
						N = 54.0×10^{-3}

N 1st Wash = 15.0×10^{-3}

N both washes = 25.0×10^{-3} .mg/cm^{2}hr$^{\frac{1}{2}}$

using calc. slopes $N_1 = 8.9 \times 10^{-3}$
$N_2 = 54.0 \times 10^{-3}$

1st wash Cu$^{(6)}$
sl p 1.81

Nail ME 2918 - aerobic corrosion (C/2)

2. 1 16.50cm Container C - 500ml
wt 146.20g - loss on corrosion removal=3.10g (saved for analysis by SEM)
av diam 1.180cm
S/Area 63.35cm^2

Description - glossy pale green over most of surface; waist at approximately 2cm from head.

hrs$^{\frac{1}{2}}$)	t (Hrs.)	Date	time	Cu (ppm)	Cl (ppm)	Pb (ppm)	1st Wash H_2O (dist)
	0	21/4	11.15				
5	49.75	23/4	1.00	0.30	6.6)		
5	217.75	30/4	1.00	0.75	12.5)		Slope = -0.46 ± 0.09 N = 3.6×10^{-3}
8	337.75	5/5	1.00	0.79	14.2)		
4	385.75	7/5		0.77	13.1)		
9	457.75	10/5		0.77	13.3)		
1	625.75	17/5		0.70	15.3)		
	649.75	18/5					
					2nd Wash KNO_3 0.2M (500ml)		
9	649.75	25/5	10.15	0 Zn	0)	.009	
0	672.50	26/5	9.00		0.45)	.009	
5	792.5	31/5	9.00	.76	2.05)		
	864.5	3/6	9.00	.91	1.54)		Slope = -0.45 ± 0.18 N = 3.6×10^{-3}

1st wash; Total Cl removed = 7.65mg
" per sq$_1$cm = 0.12
" " per hr$^{\frac{1}{2}}$ = 4.8×10^{-3}

1 and 2nd wash; 8.65 mg

using calc. slopes.

N = 3.6×10^{-3}

RAPID NAILS - FINAL WASH DITHIONATE

Wash Volume = 2 litres

$t^{\frac{1}{2}}$	t Hrs	Date-Time	$Cl_{(ppm)}$
0	0	5/5/82 12.52	0
4.47	20	6/5 9.00	1.4
6.63	44	7/5 9.00	2.1
8.25	68	10/5 9.00	0.2
9.05	82	17/5 9.00	0.3

ANNEX 3. DITHIONITE TREATMENT

Copper sheet no. I - Dithionite reduction

t. of sheet = 131.33g post 1st Wash/ wt of sludge 5.23g (3027, GT 3041, ME 2919)

/A = 340.99sq. cm. wt 125.09g

ash Volume = 2000ml post concretion removal wt = 123.73g - post 2nd wash 121.16g

Sample for analysis 5.23g 1.0025g in 250ml = 4010 ppm

$t^{\frac{1}{2}}$(hr$^{\frac{1}{2}}$)	t (hrs)	Date	time	Cl (ppm)	1st wash Dithionite
0	0	15/4	9.10am	2.0	
0.29	0.08	15/4	9.15	11	
0.40	0.16	15/4	9.20	-	
0.57	.33	15/4	9.30	2	
0.71	.50	15/4	9.40	21	Slope 17.01 ∓ 1.28 corr 0.988
0.81	0.66	15/4	10.00	1	
1.15	1.33	15/4	10.40	38	N = 0.100 ∓ 0.0075
1.68	2.83	15/4	12.00	2	
2.34	5.5	15/4	2.40	23.3,12.6	
2.67	7.16	15/4	4.20	23.1,76.6	
4.91	24.16	16/4	9.20	1.9, 6.4	
9.8	96.16	19/4	9.20	7 , 4.2	
10.96	120.16	20/4	9.20	191.4,195.	
2.0	144.16	21/4	9.20	114	- potential
13.8	192.16	22/4	9.20	47.5,57.8	5/5/82 - 1.055 mv wrt. Ag/AgCl, Kcl (sat)
14.7	216.16	23/4	9.20	9.3,17.0	= 0.853 mv vs N.H.E.
17.6	312.16	27/4	9.20	176 ,165	)
18.3	336.16	28/4	9.20	181 ,197	)
18.97	360.16	29/4	9.20	173.6,163.5	) $\bar{x}$ = 177 ∓ 14.6
21.35	456.16	3/5	9.20	169.6,173.6	)
	504.16	5/5	9.20	170.9,205.5	)
22.45	504.16	5/5	2.55	-	2nd Wash Dithionite
22.45	504.24	5/5	3.00	2.0	
22.45	504.33	5/5	3.10	0.6	
22.45	504.66	5/5	3.25	2.8	
22.47	505.00	5/5	3.45	2.28	
22.50	506.42	5/5	4.10	2.18	
22.51	506.75	5/5	4.30		
22.87	523.25	6/5	9.00	1.66	
23.04	531.25	6/5	5.00	0.30	
23.56	555.25	7/5	9.00	0.36	
25.04	627.25	10/5	9.00	0.34	
25.5	651.25	11/5	9.00	-	
28.2	795.25	17/5	9.00	0.32	

Analysis of sludge - Cu 2092, Pb 38.5, Sn 486, Zn 175, Mg N/A, Ca N/A, Sb 5.49 ppm

Liquor (ppm) - Cu - 0.1, Pb - 2, Sn 60.29, Zn N/D, Sb 4.3 ppm

Total Cl - release - 354mg Ag 9.1 ppm(sludge)

Normalised percentages

Sludge	Cu	Zn	Sn	Pb	Sb	Ca	Mg	Ag
	79.7%	.07%	18.6%	1.47%	0.17%	0.17%	3.37%	0.23%

Liquor Contained Cu 0.2mg; Pb 4mg; Sn 120.6mg Sb 8.6mg

Copper Sheet No. II Gilt Dragon - Dithionite reduction
GT 3027, GT 3039

of sheet = 404.90g   Post wash = 397.68g   wt of sludge = 3.03g recovered
S/A = 991.26 cm^2
ı Volume = 2.4 litres   Sample for analysis = 1.0001 g
in 250ml = 4.0004 ppm

ır$^{\frac{1}{2}}$)	t (hr)	Date	time	Cl (ppm)	1st Wash
	0	5/5	3.30	2.0	Slope = 36.32 ∓ 7.76 ppm.hr$^{-\frac{1}{2}}$
36	0.13		3.38	73.2	N = 0.093 ∓ 0.019 mg/cm^2/t$^{\frac{1}{2}}$
6	0.33		3.50	112.0	
8	0.66		4.10	115.2	
2	1.33		4.50	147.0	
2	17.50	6/5	9.00	201.1	
8	23.50	6/5	3.00	252	
4	41.50	7/5	9.00	264)	
6	113.50	10/5	9.00	278) $\bar{x}$ = 270.75	
7	137.50	11/5	9.00	281)	
7	161.50	12/5	9.00	260)	
8	281.50	17/5	9.00	249	

lysis:

uor : Cu: 0.18 Pb: 1.35 Sn: 1.96 Zn: N/D Ca: N/A Mg: N/A
Sb: 3.15 (ppm)
Ag: <0

dge: Cu: 2880 Pb: 110 Sn: 2.88 Zn: N/D Ca: N/A Mg: N/A
Sb: 1.97 (ppm)
Ag: 18.5ppm

al chloride released = 649.8mg

	Cu	Pb	Sn	Zn	Sb	Ag
ised tages	95.5%	3.64%	0.095%	0%	0.066%	0.61%
ıed	0.4,	3.44,	4.70,	N/D,	7.56,	N/D, mg

Nails ME 2918 Aerobic corrosion

3\. l = 147 cm
wt = 200.27g - wt of sludge = 1.02g Final wt. 198.00g
av diam = 1.3 87 cm *
S/A = 67.075 Sample retained for analysis - SEM only
h Volume = 500. cm^2

$hr^{\frac{1}{2}}$	thr	Date	time	Cl ppm 1st Wash Dithionite (500ml
	0	21/4	1.00pm	0.2
92	48	23/4	1.00pm) 1.00pm)	+ filter / 7.4 washings
96	168	28/4		192
97	264	3/5		(220.7, 202.0) (186.7, 201.9) $\bar{x}$ = 202.5 ∓ 12.06
33	336	5/5		217.9, 220.7 $\bar{x}$ 219.3 ∓ 1.4
59	384	7/5		203, 203
45	504	12/5		211.8, 215 $\bar{x}$ = 213.4 ∓ 1.6
98	624	17/5		202.6, 203.0 Final ∓ 202.8 ∓ 0.2

209.4

Total chloride released = 104.75mg

by calc. slope = 14.5 ∓ 8.47

N = $0.108 mg/cm^2 hr^{\frac{1}{2}}$ ∓ 0.0630 previously treated - Incralac removed.

wt. 2753.74g   Wash   Volume = 4 litres

$t_{\frac{1}{2}}$ hrs	t hrs/	Date	time	Cl ppm	Cu ppm	Zn ppm	Pb ppm	pH	Ag ppm
0	0	18/5	4.45	1.3	0.02	0.082	0.4	8.06	
4.1	17	19/5	9.45	3.4	3.78	13.6	1.3	7.60	
6.5	42.55	20/5	11.00	5.1	6.9	37.3			
8.2	67.25	21/5	11.30	9.4	9.6	57.7	3.3	7.39	
11.8	139.25	24/5	11.15	21.9		119.6			
12.0	143.15	24/5	3.00	44.7	12.6	197.2,177	6.7	+40g Hexammine	(6.15) 7.40 (7.01)
12.7	161.15	25/5	9.00	40.6	14.4	184	7.0	7.30	
13.0	169.15	25/5	5.00	41.9	14.2	186.4	7.0	7.32	
13.6	184.45	26/5	8.30	41.3	12.0	207.5	7.0	7.30	
14.48	209.95	27/5	9.30	44.2		176.6		7.20	
14.48	209.95	27/5	12.30	-	-	- Sn	(ppm)	13.7	2nd Wash Dithionite Volume=25 litres
~~22.31~~ 16[illegible]	498 280.[illegible]	8/6	12.30	153	0.3	.081 12.6			Ni N/D; Surface Potential - 1.074 mv wrt Ag/Ag Cl, sat KCl = 0.872 mv vs NHE

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ANNEX 3. DITHIONITE TREATMENT

Copper Sheet No. 1 – Dithionite reduction

. of sheet = 131.33g post 1st Wash/ wt 125.09g
wt of sludge 5.23g
(3027, GT 3041, ME 2919)

A = 340.99sq. cm.

Sample for analysis 5.23g 1.0025g in 250ml = 4010 ppm

sh Volume = 2000ml post concretion removal wt = 123.73g – post 2nd wash 121.16g

$\frac{1}{2}$(hr$^{\frac{1}{2}}$)	t (hrs)	Date time	Cl (ppm)	1st wash Dithionite
	0	15/4 9.10am	2.0	
.29	0.08	15/4 9.15	11	
.40	0.16	15/4 9.20	-	
.57	.33	15/4 9.30	2	
.71	.50	15/4 9.40	21	Slope 17.01 ∓ 1.28 corr 0.988
.81	0.66	15/4 10.00	1	
.15	1.33	15/4 10.40	38	N = 0.100 ∓ 0.0075
.68	2.83	15/4 12.00	2	
.34	5.5	15/4 2.40	23.3,12.6	
.67	7.16	15/4 4.20	23.1,76.6	
.91	24.16	16/4 9.20	1.9, 6.4	
.8	96.16	19/4 9.20	7 , 4.2	
.96	120.16	20/4 9.20	191.4,195.	
.0	144.16	21/4 9.20	114	– potential
.8	192.16	22/4 9.20	47.5,57.8	5/5/82 – 1.055 mv
.7	216.16	23/4 9.20	9.3,17.0	wrt. Ag/AgCl, Kcl (sat)
.6	312.16	27/4 9.20	176 ,165	) = 0.853 mv vs N.H.E.
.3	336.16	28/4 9.20	181 ,197	)
.97	360.16	29/4 9.20	173.6,163.5	) $\bar{x}$ = 177 ∓ 14.6
.35	456.16	3/5 9.20	169.6,173.6	)
	504.16	5/5 9.20	170.9,205.5	)
.45	504.16	5/5 2.55	-	
.45	504.24	5/5 3.00	2.0	2nd Wash Dithionite
.45	504.33	5/5 3.10	0.6	
.45	504.66	5/5 3.25	2.8	
.47	505.00	5/5 3.45	2.28	
.50	506.42	5/5 4.10	2.18	
.51	506.75	5/5 4.30		
.87	523.25	6/5 9.00	1.66	
.04	531.25	6/5 5.00	0.30	
.56	555.25	7/5 9.00	0.36	
.04	627.25	10/5 9.00	0.34	
5	651.25	11/5 9.00	-	
2	795.25	17/5 9.00	0.32	

alysis of sludge – Cu 2092, Pb 38.5, Sn 486, Zn 175, Mg N/A, Ca N/A, Sb 5.49 ppm

uor (ppm) – Cu – 0.1, Pb – 2, Sn 60.29, Zn N/D, Sb 4.3 ppm

al Cl – release – 354mg Ag 9.1 ppm (sludge)

malised percentages

dge	Cu	Zn	Sn	Pb	Sb	Ca	Mg	Ag
	79.7%	.07%	18.6%	1.47%	0.17%	0.17%	3.37%	0.23%

uor Contained Cu 0.2mg; Pb 4mg; Sn 120.6mg Sb 8.6mg

Nails ME 2918 Aerobic corrosion

3. l = 147 cm
wt = 200.27g - wt of sludge = 1.02g   Final wt. 198.00g
av diam = 1.3 87 cm   *
S/A = 67.075   Sample retained for analysis - SEM only
Volume = 500. cm^2

$r^{\frac{1}{2}}$	thr	Date	time	Cl ppm	1st Wash Dithionite (500ml
	0	21/4	1.00pm	0.2	
2	48	23/4	1.00pm)	+ filter/ 7.4	
			1.00pm)	washings	
5	168	28/4		192	
7	264	3/5		(220.7, 202.0) (186.7, 201.9) $\bar{x}$ = 202.5 ∓ 12.06	
3	336	5/5		217.9, 220.7 $\bar{x}$ 219.3 ∓ 1.4	
9	384	7/5		203, 203	209.4
5	504	12/5		211.8, 215 $\bar{x}$ = 213.4 ∓ 1.6	
8	624	17/5		202.6, 203.0 Final ∓ 202.8 ∓ 0.2	

Total chloride released = 104.75mg

by calc. slope = 14.5 ∓ 8.47

N = 0.108mg/cm^{2}hr$^{\frac{1}{2}}$ ∓ 0.0630 ils ME 2918 - Aerobic corrosion (E/1)

1 16.3 5cm Container E (1000ml)
wt 150.72g
diam 1.2 26cm
/Area 65.33cm^2

scription - glossy pale green; slightly offset head

½	t Hrs	Date	time	Cu ppm	Cl ppm	Pb ppm	1st Wash (1% sesquicarbonate)
0	0	21/4	11.15				Slope = 0.58
7.05	49.75	23/4	1.00	8.3	7.9		± .21
4.75	217.75	30/4	1.00	20.7	11.9		N = 8.9 x 10^{-3}
8.38	337.75	5/5	1.00	25.5	10.8		
9.64	385.75	7/5	1.00	34.8	11.6		
1.39	457.75	10/5	1.00	35.5	12.9		
5.01	625.75	17/5	1.00	38.8	21.0,		
	649.75	18/5					
					2nd Wash - (KNO$_3$ 0.2M) 500ml		
5.49	" "	25/5	10.15	0	0	.009	
5.90	672.50	26/5	9.00	.04	0.7	.009	
8.15	792.5	31/5	9.00		16.07		Slope = 7.01
9.4	864.5	3/6	9.00		27.16		± 0.50
							N = 54.0 x 10^{-3}

N 1st Wash = 15.0 x 10^{-3}

N both washes = 25.0 x 10^{-3}.mg/cm^{2}hr$^{\frac{1}{2}}$

using calc. slopes N_1 = 8.9 x 10^{-3}
N_2=54.0 x 10^{-3}

1st wash Cu$^{(6)}$
sl p 1.81

Nail ME 2918 - aerobic corrosion (C/2)

No 2. 1 16.50cm Container C - 500ml
wt 146.20g - loss on corrosion removal=3.10g (saved for analysis by SEM)
av diam 1.180cm
S/Area 63.35cm^2

Description - glossy pale green over most of surface; waist at approximately 2cm from head.

$t^{\frac{1}{2}}$ (hrs$^{\frac{1}{2}}$)	t (Hrs.)	Date	time	Cu (ppm)	Cl (ppm)	Pb (ppm)	1st Wash H_2O (dist)
0	0	21/4	11.15				
7.05	49.75	23/4	1.00	0.30	6.6)		
14.75	217.75	30/4	1.00	0.75	12.5)		Slope = 0.46
18.38	337.75	5/5	1.00	0.79	14.2)		±0.09
19.64	385.75	7/5		0.77	13.1)		N = 3.6×10^{-3}
21.39	457.75	10/5		0.77	13.3)		
25.01	625.75	17/5		0.70	15.3)		
	649.75	18/5					
					2nd Wash KNO_3 0.2M (500ml)		
25.49	649.75	25/5	10.15	0 Zn	0)	.009	
25.90	672.50	26/5	9.00		0.45)	.009	
28.15	792.5	31/5	9.00	.76	2.05)		
29.4	864.5	3/6	9.00	.91	1.54)		Slope = 0.45 ±0.18 N = 3.6×10^{-3}

1st wash; Total Cl removed = 7.65mg
" per sq cm = 0.12
" " per hr$^{\frac{1}{2}}$ = 4.8×10^{-3}

1 and 2nd wash; 8.65 mg

using calc. slopes.

N = 3.6×10^{-3}

Nail: 4 **Container:** G

Descr: Heavily concreted/grey/black appearance/pointed/bent

l = 24.10cm
wt = 776.89g
av diam = 2.35cm
S/Area = 186.2cm^2

wt loss on acid treatment: N/A

Final wt: 776.80g

$t^{\frac{1}{2}}$	hrs	Date	time	t Hrs		Cu ppm	Cl ppm	pH ppm	
	0	15/2	1.00pm		0	-	-		Wash soln. contaminate pH 13.95
	1	15/2	2.00pm		1	.21	0.8		
	1.56	15/2	3.45pm		2.45	.24	-		
	4.3	16/2	9.00am		19	.40	8.6		
	5	16/2	4.00pm		25	.53	-		
	8.18	18/2	9.00am		67	-	16.2		
	9.54	19/2	9.00am		91	-	19.3		
	11.2	22/2	9.00am		125	1.7	23.2	9.82	
	13.2	24/2	9.00am		174	1.6	26.5	9.89	
	14.9	26/2	9.00am		222	1.8	29.0	9.75	
	17.9	2/3	9.00am		320	0.9	34.2	10.72	
	19.2	4/3	9.00am		367	-	46.1		
4.8	19.7	5/3	9.00am	24	391	1.1	-		2nd Wash New soln. 1% sesquicar pH 10.05
9.7	21.5	8/3	9.00am	96	463	2.1	16.5* 8.5		
12.	22.6	10/3	9.00am	144	511	3.6	22.1*12.8		
13.8	23.6	12/3	9.00am	192		4.5	24.5*14.2	Zn	
16.2	25.1	15/3	9.00am	264	631	5.4	26.6	0.16	
" "	*		*			-	15.4*		
17.7	26.0	17/3	9.00am	312	678	4.8	16.9	-	
19.0	26.9	19/3	9.00am	360	727	5.6	15.4	-	
20.8	28.2	22/3	9.00am	432	799	6.9	17.4		
24.5	31.0	29/3	9.00am	600	967	7.32	17.5	-	
26.4		2/4	10.00am	654		-	-		1000ml 3rd W pH 9.82 1% sesquicar
26.9		5/4		726		3.96	8.05		
28.2		7/4		798		4.2	8.1		
30.7		14/4		942		4.3	9.2		
34.0		23/4		1156		-	-		
36.4		30/4		1324		3.45	5.8		
44.6		17/5		1732		4.16	8.5		

Normalized Data -

	Cl$^-$	Cu
1st wash	11.7	0.42
2nd wash	9.6	1.74
3rd wash		

Slopes:

Cl	Cu
2.21 ∓ 0.16	0.08 ∓ 0.
1.82 ∓ 0.52	0.33 ∓ 0.
-0.04 ∓ 0.12	

ME 5223 Anaerobic : Alk. Rochelle treated

ail 5.

ontainer A   Final wt. 619.23g

olume 1000   1   26.15 m

wt   641.68g

av diam   2.09cm

S/Area   188.7cm²

escription: Dark friable patina
striations visible

½ (hrs½)	t Hrs.	Date	Time	Cu ppm	Cl ppm	1st Wash 1000ml	
	0	15/2	1.00pm				
	1		2.00pm	1)	1		
.56	2.75		3.45pm	1.9)	0.5		
.3	19	16/2	9.00	2.03)	-		
.	25		4.00	4.82)	2.03		
.18	67	18/2	9.00	-)		pH	
.54	91	19/2		4.4)	-		
.2	125	22/2		5)	-	10.20	
.2	174	24/2		3.5)	1.8	10.13	
.9	222	26/2		4.3)	0.2	10.32	
.9	320	2/3		1.5)	0.2	10.69	
.2	367	4/3		)	1.6	-	
						2nd Wash (1000ml	
.8	24	5/3		0.4)	1.6)	1.1*)	
.7	96	8/3		1.9)	8.1)	5.8*)	
	144	10/3		2.8)	17.4)	12.4*)	
.8	192	12/3		3.7)	18.7	13.2*)	Zn ppm
.2	264	15/3		5.5)	17.9		
.2*	264	15/3*		-)	12.3 *		0.24
	312	17/3		5.95)	12.8		-
.0	360	19/3		6.6)	12.3		
.8	432	22/3		7.4)	13.5		
.5	600	29/3		11.4)	13.2		
.6	654	31/3	3.00	)		Combined Wash (ACE) S/A = 371.84 cm²	
.4	697	2/4		-)	-		
.7	769	5/4		2.2)	14.3?		
.5	816.9	7/4		3.5)	11.6)		
.3	978.9	14/4		5.0)	14.2)		
.6	111.9	23/4		6.8)	19.1)		
.9	1367	30/4		8.9)	22.9)		
.1	1775	17/5		9.1)	23.9	- ppte of blue green material	
.4	2157	2/6		)	17.3		

t wash

(8) slp = 0.20 $\mp$ .08
N = 1.07 $\mp$ 10^{-3}
106

d Wash

(4) slp = 1.43 $\mp$ 0.25 (corrected data*)
N = 7.6 x 10^{-3}

(4) slp = 2.01 $\mp$ .36 (raw data)
N = 10.8 x 10^{-3}

(8) slp = 0.54 $\mp$ .05
N = 2.9 x 10-3

3rd wash (ACE)

$Cl_{(4)}$ slp = 1.36 $\mp$ 0.11
N = 3.66 x 10^{-3}

$Cu_{(6)}$ slp = 0.49 $\mp$ 0.08
N = 1.32 x 10^{-3}

Nail: 1a **Container:** F l = 8.30cm

wt = 222.23g
av diam = 2.066 cm
S/Area = 60.55 cm^2

wt loss on acid treatment -1.13g
Final wt 221.00g

Descr: Dark patina/large pits.

$t^{\frac{1}{2}}$		Date	time	t Hrs		Cu ppm	Cl ppm	pH	
									1st Wash 1% sesquicarbonate solution
	0	15/2	1.00pm	0		0	0		
	1	15/2	2.00pm	1		0.14	1		
	1.56	15/2	3.45pm	2.45		0.14	-		
	4.3	16/2	9.00am	19		0.20	-		
	5	16/2	4.00pm	25		0.32	-		
	8.18	18/2	9.00am	67		-	0.6		Wash soln. contaminated; pH 13.95
	9.54	19/2	9.00am	91		0.9	-		
	11.2	22/2	9.00am	125		1.0	0.4	9.55	
	13.2	24/2	9.00am	174		0.5	0.6	10.49	
	14.9	26/2	9.00am	222		0.6	-0	10.10	
	17.9	2/3	9.00am	320		0.4	-0	11.92	
	19.2	4/3	9.00am	367		0.8	-0		2nd Wash New solution 1% sesquicarbonate; pH 10.05
4.8	19.7	5/3	9.00am	24	391	0.2	0.82		
9.7	21.5	8/3	9.00am	96	463	1.2	5.1		
12	22.6	10/3	9.00am	144	511	2.3	15.1		
13.8	23.6	12/3	9.00am	192		2.5	15.2		
16.2	25.1	15/3	9.00am	264	631	4.5	14.4		Zn/0.7 ppm
16.2	- *		*				12.4*		
17.7	26.0	17/3	9.00am	312	678	4.4	12.6		0.7
19.0	26.9	19/3	9.00am	360	727	4.9	12.4		
20.8	28.2	22/3	9.00am	432	799	6.0	11.5		0.7 1000ml 3rd Wash; pH 9.82 1% sesquicarbonate
24.5	31.0	29/3	9.00am	600	967	7.38	15.36		
		31/3							
26.4		2/4	10.00am	654		-	-		
26.9		5/4	10.00am	726		0.7	0.0		
28.2		7/4	10.00am	798		0.1	0.3		
30.7		14/4	10.00am	942		2.0	0.7		
34.0		23/4	10.00am	1156		2.3	0.3		
36.4		30/4	10.00am	1324		2.3	0.0		

Normalized Data:-	Cl^-	Cu	Slopes:- Cl	Cu	
1st Wash	-	-	0.06 ∓ 0.2	0.06	
2nd Wash	17.28×10^{-3}	3.76×10^{-3}	1.74 ∓ .46	0.38	∓ 0.03
3rd Wash		2.87×10^{-3}	0.18*	0.29	∓ 0.12

(3 *points only)

Nail: 3 **Container:** E

l = 19.5cm
wt = 474.50g
av diam = 1.86cm
S/Area = 118.74cm^2

wt loss on acid treatment: -11.25g

Final wt: 463.24g

Descr: Heavy dark encrustation incorporating small calcareous remains overlying deeply pitted areas. Streations visible on rest of surface which was smooth and shiney and only lightly patinated.

t½		Date	time	t	Hrs	Cu ppm	Clppm	pH		1000ml 1st Wash
	0	15/2	1.00pm		0	-	-			1 % sesquicarbonate
	1	15/2	2.00pm		1	0.2	0.6		Zn (ppm) 0.35	
	1.56	15/2	3.45pm		2.45	0.2	1.0			
	4.3	16/2	9.00am		19	0.2	-			
	5	16/2	4.00pm		25	0.3	1.3			Wash soln. contaminated; pH 13.95
	8.18	18/2	9.00am		67	-	1.5			
	9.54	19/2	9.00am		91	0.7	-			
	11.2	22/2	9.00am		125	0.9	2.1	9.56		
	13.2	24/2	9.00am		174	0.8	2.2	10.20		
	14.9	26/2	9.00am		222	0.9	-	9.82		
	17.9	2/3	9.00am		320	0.4	-	10.78		
	19.2	4/3	9.00am		367	-	2.1	-		
4.8	19.7	5/3	9.00am	24	391	0.7	2.07			1000ml 2nd Wash New soln. 1% sesquicarb. pH 10.05
9.7	21.5	8/3	9.00am	96	463	1.4	11.00			
12.	22.6	10/3	9.00am	144	511	2.5	14.8			
13.8	23.6	12/3	9.00am	192		3.0	15.7			
16.2	25.1	15/3	9.00am	264	631	5.2	14.3		Zn (ppm) 0.6	
11.11	*		*				13.1*		-	
17.7	26.0	17/3	9.00am	312	678	5.2	17.7*		0.58	
19.0	26.9	19/3	9.00am	360	727	5.8	19.0*		-	
20.8	28.2	22/3	9.00am	432	799	7.8	20.8*		0.67	
24.5	31.0	29/3	9.00am	600	967	9.3	24.5*		-	Combined wash ACE
26.4		2/4	10.00am	654						1000ml 3rd Was pH 9.82 1% sesquicarb.
26.9		5/4		726						
28.2		7/4		798						
30.7		14/4		942						
34.0		23/4		1156						
36.4		30/4		1324						

Normalized Data -	Cl$^-$	Cu	Slopes: Cl	Cl
1st wash	1.0		0.12 ± .01	0.03 + 0.02
2nd wash	12.1	3.9	1.44 ± .15	0.47 ± .04
3rd wash				

Nail: 1b **Container:** D

1 = 14.36cm
wt = 282.54g
av diam = 1.67cm
S/Area = 79.75cm²

wt loss on acid treatment: -1.95g

Final wt: 280.5g

Descr: Dk friable patina over dk surfaces/ wrought pattern visible/pointed/ some tenacious concretions/no deep pitting

t½	Hrs	Date	time	t Hrs		Cl ppm	Cl ppm	pH	600ml 1st Wash
	0	15/2	1.00pm		0			Zn 0.4	(ppm)
	1	15/2	2.00pm		1				
	1.56	15/2	3.45pm		2.45				
	4.3	16/2	9.00am		19				
	5	16/2	4.00pm		25				
	8.18	18/2	9.00am		67				Wash soln. contaminated; pH 13.95
	9.54	19/2	9.00am		91				
	11.2	22/2	9.00am		125				
	13.2	24/2	9.00am		174				
	14.9	26/2	9.00am		222				
	17.9	2/3	9.00am		320				
	19.2	4/3	9.00am		367				
4.8	19.7	5/3	9.00am	24	391				600ml 2nd Wash New soln. 1% sesquicarb. pH 10.05
9.7	21.5	8/3	9.00am	96	463				
12.	22.6	10/3	9.00am	144	511				
13.8	23.6	12/3	9.00am	192					
16.2	25.1	15/3	9.00am	264	631			Zn 0.6	(ppm)
11.14	*		*						
17.7	26.0	17/3	9.00am	312	678			0.6	
19.0	26.9	19/3	9.00am	360	727				
20.8	28.2	22/3	9.00am	432	799			0.7	
24.5	31.0	29/3	9.00am	600	967				
26.4		2/4	10.00am	654					1000ml 3rd Was pH 9.82 1% sesquicarb.
26.9		5/4		726					
28.2		7/4		798					
30.7		14/4		942					
34.0		23/4		1156					
36.4		30/4		1324					

Normalized Data –	Cl⁻	Cu	Slopes:	Cl	Cu
1st wash					
2nd wash	11.50	4.50		1.84 ∓ 0.16	0.45 ∓ 0.05
3rd wash	–	5.38			0.43 ∓ 0.02

Nail: 2a   **Container:** C   1 = 11.44cm   **wt loss on acid treatment:** -5.49g
wt = 213.14g
av diam = 1.73cm   **Final wt:** 207.48 (ie + .03g)
S/Area = 66.90cm^2

Descr: Dark friable material over dark patina/some tenacious concretions overlying deep pitting/waisted shape with obvious striation

$t_{\frac{1}{2}}$		Date	time	t (Hrs)		Cu (ppm)	Cl (ppm)		pH	600ml 1st Wash
	0	15/2	1.00pm		0	-	-		Zn 0.3	(ppm)
	1	15/2	2.00pm		1	-	-			
	1.56	15/2	3.45pm		2.45	.11	0			
	4.3	16/2	9.00am		19	.11	0.4			
	5	16/2	4.00pm		25	.13	-			Wash soln. contaminated; pH 13.95
	8.18	18/2	9.00am		67	.30	2.6			
	9.54	19/2	9.00am		91	.14	1.4			
	11.2	22/2	9.00am		125	.6	3.8		9.72	
	13.2	24/2	9.00am		174	.6	3.3		9.80	
	14.9	26/2	9.00am		222	.9	4.0		9.72	
	17.9	2/3	9.00am		320	.4	2.1		10.81	
	19.2	4/3	9.00am		367	-	-		-	
4.8	19.7	5/3	9.00am	24	391	0.4	4.74			500ml 2nd Wash New soln. 1% sesquicarb pH 10.05
9.7	21.5	8/3	9.00am	96	463	0.8	27.1	8.35		
12.	22.6	10/3	9.00am	144	511	1.2	13.8			
13.8	23.6	12/3	9.00am	192		2.4	14.2			
16.2	25.1	15/3	9.00am	264	631	4.3	12.5		Zn 0.6	
11.11	*		*				11.9*		-	
17.7	26.0	17/3	9.00am	312	678	5.0	11.6		0.6	
19.0	26.9	19/3	9.00am	360	727	5.8	11.9		-	
20.8	28.2	22/3	9.00am	432	799	7.8	16.9		0.6	
24.5	31.0	29/3	9.00am	600	967	11.6	12.2		-	
26.4		2/4	10.00am	654						Combined Wash container "A" 1000ml 3rd Wa pH 9.82 1% sesquicar
26.9		5/4		726						
28.2		7/4		798						
30.7		14/4		942						
34.0		23/4		1156						
36.4		30/4		1324						

Normalized Data - x 10^{-3}	Cl^-	Cu	Slopes:	Cl	Cu
1st wash	-	-		-	-
2nd wash	8.4	6.54			
3rd wash ACE combined, wash see sheet "A"				1.13 ∓ 0.22	0.73 ∓ 0.06

DATA SUMMARY SHEET   ME 5223

Nail: 2(b)   **Container:** B

l = 12.00 cm
wt = 282.24g
av diam = 1.95cm
S/Area = 79.46 sq.cm^2

wt loss on acid treatment: −3.04g

Final wt: 279.01 g

Descr: dark friable material over dark patina/generally smooth appearance/ some striations.

t½		Date	time	t hrs		Cu ppm	Cl ppm	pH	600ml 1st Wash
	0	15/2	1.00pm		0	-	-	Zn	
	1	15/2	2.00pm		1	.01	-	0.23	
	1.56	15/2	3.45pm		2.45	.11	0.4		
	4.3	16/2	9.00am		19	.13	0.5		
	5	16/2	4.00pm		25	.24	-		Wash soln. contaminated; pH 13.95
	8.18	18/2	9.00am		67	-	1.0		
	9.54	19/2	9.00am		91	.60	-		
	11.2	22/2	9.00am		125	1.30	1.1		
	13.2	24/2	9.00am		174	.60	1.2	9.62	
	14.9	26/2	9.00am		222	1.10	-	10.09	
	17.9	2/3	9.00am		320	.80	0.2	9.87	
	19.2	4/3	9.00am		367	-	-	10.20	
4.8	19.7	5/3	9.00am	24	391	1.7	6.05		600ml 2nd Wash New soln. 1% sesquicarb. pH 10.05
9.7	21.5	8/3	9.00am	96	463	1.4	10.1		
12.	22.6	10/3	9.00am	144	511	2.4	19.0		
13.8	23.6	12/3	9.00am	192		3.4	20.3	Zn	
16.2	25.1	15/3	9.00am	264	631	5.8	18.1	0.88	
11.11	*		*				17.3*	-	
17.7	26.0	17/3	9.00am	312	678	5.6	14.5	0.92	
19.0	26.9	19/3	9.00am	360	727	7.3	17.3	-	
20.8	28.2	22/3	9.00am	432	799	9.0	12.7	1.09 = .62mg	
24.5	31.0	29/3	9.00am	600	967	11.2	17.8	-	
26.4		2/4	10.00am	654		-	-		1000ml 3rd Wash pH 9.82 1% sesquicarb.
26.9		5/4		726		0.85	0.6		
28.2		7/4		798		1.56	1.8		
30.7		14/4		942		3.45	1.3		
34.0		23/4		1156		3.75	3.0		
36.4		30/4		1324		4.58	1.8		

Normalized Data -	Cl^-	Cu	Slopes: Cl^-	Cu
1st wash	0.5	0.5	0.07 ∓ .01	0.06 ∓ 0.02
[illegible]	12.2	5.1	1.61 ∓ 0.38	0.69 ∓ 0.04
[illegible]	3.5	4.8	0.28 ∓ 0.12	0.38 ∓ 0.07

ME 5223 Anaerobic : Alk. Rochelle treated A/5

Nail 5.

Container A Final wt. 619.23g

volume 1000

l 26.15 m
wt 641.68g
av diam 2.09cm
S/Area 188.7cm²

Description: Dark friable patina
striations visible

$t^{\frac{1}{2}}$ (hrs$^{\frac{1}{2}}$)	t Hrs.	Date	Time	Cu ppm	Cl ppm	1st Wash 1000ml	
0	0	15/2	1.00pm				
1	1		2.00pm	1)	1		
1.56	2.75		3.45pm	1.9)	0.5		
4.3	19	16/2	9.00	2.03)	-		
5.	25		4.00	4.82)	2.03		
8.18	67	18/2	9.00	-)			
9.54	91	19/2		4.4)	-	pH	
1.2	125	22/2		5)	-	10.20	
3.2	174	24/2		3.5)	1.8	10.13	
4.9	222	26/2		4.3)	0.2	10.32	
7.9	320	2/3		1.5)	0.2	10.69	
.2	367	4/3		)	1.6	-	
						2nd Wash (1000m	
4.8	24	5/3		0.4)	1.6)	1.1*)	
.7	96	8/3		1.9)	8.1)	5.8*)	
	144	10/3		2.8)	17.4)	12.4*)	
.8	192	12/3		3.7)	18.7	13.2*)	Zn ppm
.2	264	15/3		5.5)	17.9		
6.2*	264	15/3*		-)	12.3 *		0.24
7	312	17/3		5.95)	12.8		-
.0	360	19/3		6.6)	12.3		
.8	432	22/3		7.4)	13.5		
.5	600	29/3		11.4)	13.2		
.6	654	31/3	3.00	)		Combined Wash (ACE) S/A = 371.84 cm²	
.4	697	2/4		-)	-		
.7	769	5/4		2.2)	14.3?		
.5	816.9	7/4		3.5)	11.6)		
.3	978.9	14/4		5.0)	14.2)		
.6	111.9	23/4		6.8)	19.1)		
.9	1367	30/4		8.9)	22.9)		
.1	1775	17/5		9.1)	23.9 - ppte of blue		
.4	2157	2/6		)	17.3 green material		

t wash

(8) slp = 0.20 $\mp$ .08
N = 1.07 $\mp$ 10^{-3}
106

3rd wash (ACE)

$Cl_{(4)}$ slp = 1.36 $\mp$ 0.11
N = 3.66 x 10^{-3}

d Wash

(4) slp = 1.43 $\mp$ 0.25 (corrected data*)
N = 7.6 x 10^{-3}

$Cu_{(6)}$ slp = 0.49 $\mp$ 0.08
N = 1.32 x 10^{-3}

(4) slp = 2.01 $\mp$ .36 (raw data)
N = 10.8 x 10^{-3}

(8) slp = 0.54 $\mp$ .05
N = 2.9 x 10-3