

### Abstract

Analysis of the extent of corrosion of cast iron cannon recovered from historic shipwrecks off Australian coasts has revealed a common corrosion mechanism. Data obtained relate to cannon cast in the seventeenth and up to the nineteenth century with immersion times up to 366 years. Analysis of the kinetics of chloride ion extraction during storage and electrolysis in sodium hydroxide solutions has led to the development of a model for predicting the rate of the chloride extraction process. In-situ corrosion measurements relate the amount of water movement with the average corrosion rates and the depth of graphitisation of the cast iron cannon. Equations have been established that relate the depth of corrosion and the time taken to reach plateau levels. The amount of chloride ions removed and the rate at which the process occurs are intimately related to the nature of the shipwreck sites. Through the use of the relationships established from treatment of twenty six cannon from ten wreck sites it is now possible to calculate when treatments are likely to be completed and how much chloride ions will be able to be extracted in the conservation programme. With a knowledge of in-situ corrosion data it is now possible to establish which cannon will be in the best state of preservation prior to any recovery operation. The chloride extraction kinetics can also be used to calculate the age of unknown shipwrecks!

### Keywords

Corrosion, conservation, iron cannon, treatment kinetics, shipwrecks, sea water, dating

## Conservation of Corroded Iron Cannon and the Influence of Degradation on Treatment Times

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### Introduction

One of the problems commonly encountered with the treatment of corroded iron cannon recovered from historic shipwreck sites is that it is very difficult to predict how long the treatment will take. Many of the concerns relate to the fact that for a number of conservators the object in front of them is the first example of such a massive artefact. Since corroded iron cannon have been undergoing treatment in the laboratories of the Western Australian Museum for the last twenty years there exists a considerable data base of treatment reports. Apart from laboratory studies, data obtained from in-situ corrosion measurements on ten wreck sites has also been collected to help find answers to the questions of how to treat the cannon.

When iron cannon are immersed in the warm tropical to sub-tropical waters they become colonised with a variety of marine organisms that form a protective and encapsulating layer of calcareous material over the surface of the object. The concretion consists of a matrix of corrosion products, marine organisms and the materials resulting from their interactions as well as entrained sediments. The process of concretion formation on iron objects has been described by North<sup>1</sup>. More recently the increase in the rate of concretion formation due to the phosphorus content of the iron has been quantified<sup>2</sup>. Analysis of the thickness of calcareous materials showed that there was a linear relationship between the annual growth rate and the weight percent phosphorus in the metal. The concretion layer forms a separation barrier between the oxidation of the artefact and the reduction of dissolved oxygen.

Recent in-situ studies of corroding iron artefacts on the wreck of HMS *Sirius* (1790) have established that the corrosion of iron on shipwreck sites is largely dominated by the flux of dissolved oxygen to the concreted surface<sup>3</sup>. The physical protrusion of an object on a wreck site will therefore be of major importance in determining how much oxygenated sea water will flow past the object. For buried artefacts the anaerobic corrosion mechanism, (corrosion in the absence of oxygen) will be dominated by the cathodic processes which involve the reduction of water. The data reported in this paper relates primarily to cannon that have corroded on the seabed in well oxygenated waters.

### Results and discussion

#### *Cannon corrosion on wreck sites*

The *Batavia* (1629) wrecksite is characterised by massive wave surges as the heavy swells break over *Morning Reef* in the Houtman Abrolhos Islands located some 70 km out to sea from Geraldton, Western Australia. A series of cannon were recovered during the main excavations seasons between 1972-1976 and brought to Fremantle for conservation treatment using electrolysis in sodium hydroxide solutions. The technique is essentially the same as developed for the conservation of cannon from HMB *Endeavour* (1770)<sup>4</sup>. As part of the routine assessment of the effectiveness of the treatment process, samples of corroded metal are drilled at the initiation of the treatment and towards the end and analysed for chloride ions.

The analytical data provides the conservator with information about the extent of the degradation and about the fabrication technology. The composition of cast iron cannon results in a metallurgical structure that consists of varying

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proportions of graphite flakes in a matrix of cementite, pearlite and ferrite<sup>5</sup>. When the cannon corrodes, the phases that have the highest iron content will be preferentially oxidised and this ultimately results in a corroded zone that is essentially *graphitised cast iron*. The corroded cast iron has lost most of its original mechanical properties but it still retains the original surface details and overall dimensions. The retention of the original surface is the primary aim of the overall conservation treatment.

Apart from several cannon from the *Batavia* (1629), a total of eight cannon were recovered in 1980 from the wreck of the American China Trader *Rapid* (1811), five from the remains of the whaler *Lively* (1810), three from the *Vergulde Draeck* (1656) and individual cannon from the sites of the *Trial* (1622), *Zuytdorp* (1722), *Fairy Queen* (1875) and the *Cumberland* (1830). Since the *Rapid* site was the first at which in-situ corrosion measurements were taken<sup>6</sup>, it is useful to initially look at data from this wreck since it also had the most accessible archaeological records. In order to facilitate comparisons of the rate of corrosion on a variety of sites that have been immersed in sea water for times varying from 114 to 365 years, the corrosion data is averaged over the number of years of immersion. The annual mean depth of graphitisation is noted as  $d_g$  in units of  $\text{mm}\cdot\text{y}^{-1}$ . Since corroded cast iron retains its original dimensions, the rate of corrosion can be gauged by measuring the depth of graphitisation of the cannon. This is effected by drilling into the artefact with a 5 mm. steel bit until the resistance of the uncorroded metal is felt—the depth of penetration,  $d$ , is the depth of graphitisation.

The *Rapid* cannon provide an interesting example of how the microenvironment on the site dictates the extent of corrosion. A summary of the data is listed in table 1. In assessing the data in table 1 it is useful to note that the average long-term corrosion rate for iron in a marine environment is approximately 0.1 mm per year<sup>7</sup>.

Table 1. Corrosion depths for cannon on the *Rapid* (1811).

Location	RP4090	RP4288	RP4031	RP4205	RP4206	RP4207	RP4147	RP4032
Muzzle*	16	17	10	4	10	14	4.5	12
Cascabel*	16	15	5	4	10	10	4	8
Mean*	16	16.7 ± 1.5	7.5 ± 3.5	4	10	12.0 ± 2.8	4.25 ± 0.4	10.0 ± 2.1
Annual $d_g$	0.096	0.101	0.045	0.024	0.059	0.072	0.026	0.059

\* Corrosion/graphitisation depths measured in mm.

Inspection of the data in table 1 shows that two cannon from the *Rapid* had the "average" corrosion rate for an open ocean site. The wreck lies in seven metres of water inside an offshore reef and at the time of the initial site inspection only one cannon was seen lying proud of the sea bed. It is this cannon (RP4288) which is the most extensively graphitised. The carronade (RP 4090) with the higher corrosion rate was found under a mound of ballast. There were a significant number of copper artefacts located on the site in the general vicinity of the carronades. There were upwards of 850 copper artefacts within a two metre grid line found 6–8 metres from the guns. Copper fastenings in close proximity to the cannon showed significantly less corrosion than those artefacts further away.

Previous studies on the corrosion phenomena on this site<sup>8,9</sup> and on the site of the *Hadda* in the Abrolhos Islands<sup>10</sup> have confirmed the existence of proximity corrosion which is a form of long-range galvanic coupling. Such phenomena may be the underlying cause for the increased corrosion rate for the carronade RP 4090. Three other cannon were partially exposed on the seabed and they exhibited the next highest corrosion rate with an average value of the mean annual depth of graphitisation being  $0.064 \pm 0.007 \text{ mm}\cdot\text{year}^{-1}$ . Two of the cannon (RP 4206 & 4207) were a "crossed pair", i.e. they were found concreted together in a scissor formation.

The other two cannon (RP4147 & RP4205) and the two carronades (RP 4031 & RP 4090) were found under the mound of ballast stones and amongst the general wreckage of the vessel. The two buried cannon had an average annual mean corrosion rate of  $0.025 \pm 0.001$  while the carronades had rates of 0.045 and  $0.096 \text{ mm} \cdot \text{year}^{-1}$ . Site excavation records are incomplete but the divers notes indicated that the carronades were placed at a higher level in the *sediment* than the cannon and this is reflected in the higher levels of corrosion. Generally it can be seen that, in the absence of specific effects of galvanic coupling, there is a lowering of the rate of corrosion with the increasing depth of burial on the site. This is primarily a reflection of the decreased amount of water movement combined with lower concentrations of dissolved oxygen.

Only one cannon (RP4205) had its corrosion potential ( $E_{\text{corr}}$ ) recorded on-site. The  $E_{\text{corr}}$  value was  $-0.412$  volts (1) which indicated that it was corroding at a relatively slow rate. Using the relationship between  $E_{\text{corr}}$  values and corrosion on wreck sites<sup>3</sup>, the calculated depth of corrosion was  $0.034 \text{ mm} \cdot \text{y}^{-1}$ . The calculated value is within the range of the standard deviation of the observed rate of  $0.024 \text{ mm} \cdot \text{y}^{-1}$ .

The wreck of the *Lively* (c.1820) on the Rowley Shoals is characterised by a scattered deposit of metallic remains. No wooden structure remains and this is consistent with the much higher energy of the site. The wreck lies in a gully on the edge of a coral atoll and the water depth varies from seven to zero metres at the reef top. The corrosion parameters for the five cannon recovered from the site are listed below in table 2.

Table 2. Corrosion parameters for cannon from the *Lively* (1810).

Location	RS125	RS24	RS25	RS26	RS 124
Muzzle*	16	14	14	10	18
Cascabel*	12	14	10	10	16
Mean value*	$14 \pm 2.8$	$14.3 \pm 0.6$	$12.0 \pm 2.8$	10	$17.0 \pm 1.4$
Annual $d_p$	0.085	0.089	0.075	0.062	0.106
$E_{\text{corr}}$ , volts	-0.200	-0.262	-0.273	-0.252	-0.219

\* Corrosion/graphitisation depths measured in mm.

Analysis of the corrosion potential data shows that there is a linear relationship between the corrosion potentials ( $E_{\text{corr}}$ ) and the logarithm of the average annual rate of graphitisation, i.e.  $\log d_p$ . The *in-situ*  $E_{\text{corr}}$  values of the cannon fall into two sets of data which have the same slope for the  $E_{\text{corr}}$  vs.  $\log d_p$  plots but different intercepts. The equation is

$$\log d_p = 2.34 E_{\text{corr}} - 0.459 \quad 1$$

for the cannon RS 24,25 & 124. For the RS 125 and RS 26 the intercept is  $-0.603$ . It is possible that the difference in intercepts is due to some chemical or metallurgical difference in the cannon or that the nature of the water movement around these objects is different.

This logarithmic dependence of corrosion rate on the  $E_{\text{corr}}$  of the metal is consistent with corrosion phenomena that are under electrochemical control<sup>3</sup>. Each site will present a different range of corrosion microenvironments but since there is a direct linear relationship between the logarithm of the corrosion rate, as measured by  $\log d_p$ , and the  $E_{\text{corr}}$  value, it is now possible to see which cannon is the most/least corroded and so make the best archaeological decisions involving recovery.

Although no *in-situ* corrosion measurements have been made to date on the *Batavia*, the cannon recovered from the site have provided a useful set of ordnance that is generally extensively corroded. The physical nature of a shelving gully on the edge of a reef is typical of a high energy site characterised by large volumes of water flowing over the area with significant velocity. Large waves break heavily on the site during heavy ocean swells associated with storms etc.

Table 3. Depths of graphitisation of iron cannon from the wreck of the *Batavia* (1629).

Artefact no.	BAT 8731†	BAT 8722†	BAT 8723	BAT 8720	BAT 8724	BAT 8726	BAT 80309
Muzzle*	53	—	33	23	—	32	—
Cascabel*	63	44	54	48	29.2	16	18
Mean*	58 ± 7.1	44	43.5 ± 14.8	35.5 ± 17.7	29.2	24 ± 11.3	18
Annual $d_p$	0.167 ± 0.20	0.126	0.125 ± 0.043	0.102 ± 0.051	0.084	0.069 ± 0.033	0.052

\* Corrosion/graphitisation depths measured in mm.

† The two cannon BAT 8731 & 8722 were both found broken on the wreck site.

It is not unexpected to find depths of graphitisation up to an mean value of 58 mm after more than 350 years of exposure to such conditions.

Although the range of average corrosion rates on the *Batavia* site is considerable, the variation from 0.167 – 0.052 mm·y<sup>-1</sup> is of the same order as the range of rates found on the *Rapid* site. The major cause of variation on the *Batavia* site is the topography of the seabed which is full of local gullies and the piles of sandstone building blocks which resulted in localised turbulence. The smaller variations in  $d_p$  values observed for the cannon on the site of the *Lively* is due to the more localised distribution of the cannon. The average of the  $d_p$  values for the *Batavia*, *Lively* and *Rapid* sites are 0.104±0.039, 0.083±0.016 and 0.060±0.029 mm·y<sup>-1</sup> respectively. The shallower average water depth and the location of the *Batavia* and *Lively* sites on the edge of reefs is the primary cause for the differing extents of corrosion.

Data on the net effects of temperature on cannon corrosion are not unambiguous. Although the concentration of oxygen increases with decreasing temperature, the diffusion coefficients fall and so this often cancels out the apparent increase in the rate of supply of dissolved oxygen to the corroding surfaces. With cooler water the extent and nature of the marine growth also changes and this in turn alters the amount of "protection" that a concretion can provide. Two cannon from the site of the *Sydney Cove* (1797) in Bass Strait provide data from a much colder site. Although the site is subject to storms, it has a sandy bottom and the average water temperature is 14.5±2.3 °C at a water depth of 3–5.5 metres<sup>11</sup>. The average graphitisation depth was 7.3±2.3 mm which gives an  $d_p$  value of 0.041 ± 0.013 mm·y<sup>-1</sup> which is similar to one of the carronades on the *Rapid* site, where the average temperature is 24.4±2.0°C<sup>6</sup>.

Another *cold* site is that of the *Cumberland* (1830) off Cape Leeuwin where the average water temperature is 18.6±1.5°C and the average annual corrosion rate was calculated at 0.028 mm·y<sup>-1</sup>. Again this corrosion rate is of the same order as two of the cannon from the *Rapid* site, where the cannon had been protected under the ballast mound. Observations on a large number of submerged iron materials indicates that the corrosion rate of concreted iron in sea water is relatively temperature independent<sup>12</sup>.

Given that a common corrosion mechanism controls the deterioration of the cannon, it is not unexpected to find correlations between the amount of chloride ions extracted during conservation and the extent of corrosion. Analysis of treatment data for ten cannon from five sites, for which complete data sets are available, shows that the total number of kilograms of chloride ions is directly related to the depth of graphitisation,  $d$ , via the relationship

$$\Sigma \text{Cl} = 0.0367 d^2 + 2.61 \quad 2$$

where  $\Sigma \text{Cl}$  is the weight of chloride ions in kg and  $d$  is the depth of graphitisation, measured in mm. Since the corrosion rate settles down to a pseudo steady-state after some years, it is not unexpected to find the parabolic relationship (equation 2) between the total amount of chloride in the cannon and the depth of graphitisation. Where cannon do not follow this relationship it is due to factors such as the *Zuytdorp* cannon having corroded only on the "outside" since the tompon in the muzzle had sealed the bore from the sea water<sup>3</sup>. Equation 2 can be used to calculate the total amount of chloride that should be extracted from concreted iron cannon that have corroded in sea water where the salinity

ranges from 34–37 parts per thousand (ppt). Such calculations are a handy guide to conservators assessing the progress of an electrolysis treatment.

#### *Chloride extraction rates*

The diffusion controlled nature of the washing process has been well documented<sup>13</sup> and it is noted that chloride ions diffuse out at a rate that is linearly dependent on the square root of the treatment time<sup>14</sup>. Once a plateau has been reached it is time to change to a fresh solution of sodium hydroxide. The chloride ions then diffuse out at a slower rate until the next plateau is reached and the solution changed again. Regular monitoring of the wash solutions of the cannon has provided the basic information as to when solutions need changing and when the treatment is complete. Many of the electrolysis times are in excess of five years. At the end of the electrolysis process the total amount of chloride ions released can be calculated from values of the plateau levels (corrected for background levels of the water) and from a knowledge of the solution volume.

We have applied the same methods of data analysis as for the desalination of copper and its alloys<sup>15</sup> where the release rates were standardised as  $x \text{ mg} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1/2}$  by multiplying the rate in ppm of chloride per hour<sup>1/2</sup> by the solution volume in litres and dividing by the geometric surface area of the cannon in  $\text{cm}^2$ . It should be noted that the contribution of surface roughness and effective porosity have been ignored in the calculations owing to our inability to accurately assess their values. The common microstructure and composition of the iron cannon means that corroded cannon are closely related in their physical properties. Analysis of the wash data for fifteen iron cannon shows that the rate of release of chloride ions is directly related to the "porosity" of the corroded metal via the relationship

$$R = 3610 d_p^2 - 0.110 \quad 3$$

where  $R$  is the chloride ion release rate in  $\text{mg} \cdot \text{cm}^{-2} \cdot \text{hr}^{-1/2}$  and  $d_p^2$  is the square of the annual average depth of graphitisation of the cannon (in  $\text{mm} \cdot \text{y}^{-1}$ ). Even though the more corroded cannon have a significantly greater amount of chloride ion in the corroded matrix, the rate of release is dependent on the tortuosity of the diffusion path.

With a knowledge of the depth of graphitisation and the time between when the vessel was wrecked and when the artefact was recovered, it is now possible using equations 2 and 3 to calculate not only the amount of chloride that can be expected to be released into the treatment solutions, but also the rate at which the ions will diffuse into the wash solutions. The relationships allow estimation of electrolysis treatment times and to assess whether or not the physical set-up of the electrolysis is optimal.

When the concentration of chloride ions at the plateau levels are compared with the total amount extracted by the end of the treatment some common relationships are found. The expressions for the percentage of chloride removed at each of the washing stages is given by the following relationships:

$$\begin{aligned} [\text{Cl}]_{\text{ext}} \text{ at first plateau} &= 65.8 \pm 2.8\% \\ [\text{Cl}]_{\text{ext}} \text{ at second plateau} &= 21.5 \pm 3.4\% \\ [\text{Cl}]_{\text{ext}} \text{ at third plateau} &= 10.6 \pm 2.9\% \end{aligned}$$

Since the total amount of chloride released after the first three solutions changes amounts, on average, to 97.9%, it can be seen that for some cannon a fourth electrolysis solution is required to complete the desalination.

In planning the treatment of cannon it is often useful to have an estimate of how long it will take before it is necessary to change the wash solutions. Analysis of the corrosion and washing data shows that there is a relationship between the extent of corrosion and the time it takes to reach the first and subsequent plateaus. The general form of the equation is

$$t_n = k_n/d_p \quad 4$$

where  $t_n$  is the amount of time (in days) to reach the  $n^{\text{th}}$  plateau,  $d_p$  is the annual

depth of graphitisation of the cannon (in  $\text{mm}\cdot\text{y}^{-1}$ ) and  $k_n$  is a constant for the  $n^{\text{th}}$  plateau. The values for the plateau constants are  $k_1 = 33.9 \pm 5.6$ ,  $k_2 = 68.5 \pm 20$  and  $k_3 = 103 \pm 45 \text{ days}\cdot\text{y}\cdot\text{mm}^{-1}$ . The increasing standard deviations associated with the time taken to reach the subsequent plateaus is due to the natural errors associated with the variability of the depth of corrosion over the surface of the cannon and also due to the non-standard conditions associated with the electrolysis of the cannon. **All the above relationships apply to deconcreted cannon that are undergoing electrolysis in sodium hydroxide.** The chloride extraction kinetics of the *Zuytdorp* cannon did not follow the same relationships because the tampion effectively sealed the bore of the cannon<sup>2</sup>.

#### Dating

If the date of the wreck is unknown it may be possible to use the depth of graphitisation and the chloride ion extraction rates to calculate the age of the vessel. Since the average annual depth of graphitisation  $d_g$  is obtained by dividing  $d$  by the time between sinking and recovery,  $t_w$ , equation 3 can be rearranged to give

$$d_g = \{(R+0.11)/3610\}^{1/n} = d/t_w,$$

or more simply in the form

$$t_w = 60.08 d/(R+0.11)^n \quad 4$$

The applicability of equation 4 as a dating has been used on a number of wrecks of known dates, chloride release rates and depths of graphitisation. The results are shown in table 4 where the calculated  $t_w$  dates agree with actual dates within the error range of  $-3.9 \pm 4.8\%$ . When consideration is given to all the variables associated with dating an object from kinetic data, the agreement is very good and promises to be of value to conservators and archaeologists.

Table 4. Comparison of calculated and real times of immersion of corroded iron cannon.

Vessel	R $\text{mg}\cdot\text{cm}^{-2}\cdot\text{hr}^{-n}$	d mm	$t_w$ years	$t_{\text{actual}}$ years
<i>Trial</i> 3207 (1622)	7.5	17.2	375	363
<i>Batavia</i> 80309 (1629)	11.1	18.0	323	347
<i>HMS Sirius</i> 49 (1790)	67.4	25.0	183	195
<i>Rapid</i> 4032 (1811)	14.6	10.0	157	167

#### Composition and corrosion

The composition of eight cannon from different wreck sites dating from the seventeenth to the nineteenth century have been determined by chemical analysis of core samples taken when the connections were being made for the attachment of the cathodic current cable. The data is summarised below in table 5. In general the composition of the cannon varies remarkably little from the earliest guns of the *Trial* (1622) to the wreck of the *Rapid* (1811), with typical carbon contents of  $3.66 \pm 0.7\%$ .

The asterisked values in table 5 for the *Vergulde Draeck* and the *Trial* relate to a corroded sample rather than parent metal and so the carbon content is anomalously high and is not a reflection of the basic core composition. There are two sets of typical sulphur impurity levels; one set of five cannon has average values of  $0.059 \pm 0.026\%$  and the other three  $0.20 \pm 0.09\%$ . The lower values are typical of material that was produced in a charcoal fuelled furnace<sup>3</sup>. There is sufficient manganese in all the cannon to form manganese sulphide inclusions and so effectively remove the sulphur from the metallurgy of the metal. Normally, higher sulphur levels tend to promote formation of coarser graphite flakes.

The amount of silicon for the *Sirius* (1790) carronade is very low at a value of  $0.10 \text{ wt.}\%$  compared with the average value for four of the other cannon of  $1.57 \pm 0.26\%$ . Higher silicon levels promote graphite formation and suppress carbide formation; this may account in part for the extensive corrosion of the

Table 5. Composition of cast iron ordnance recovered from historic shipwrecks.

Artefact	C	S	Si	Mn	P	Ni	Cu	Cl	Carbon eq.†
<i>Rapid</i> 4032	4.0	0.18	1.93	0.475	0.37	0.22	0.023	0.005	4.8
<i>Batavia</i> 8720	4.45	0.12	1.45	0.330	0.32	0.019	0.007	1.95	5.0
<i>Cumberland</i>									
52	2.90	0.075	1.57	0.275	0.30	0.013	0.016	<0.005	4.7
<i>Trial</i> 3207	9.4*	0.30	2.54	0.315	0.74	0.019	0.013	1.31	n.a.
<i>Fairy Queen</i>									
3516	2.80	0.015	3.13	1.30	1.04	0.021	0.011	0.0002	4.2
<i>Vergulde</i>									
<i>Draeck</i>									
2435	6.85*	0.070	1.33	0.76	0.40	0.012	0.006	<0.0002	n.a.
<i>Zuytdorp</i>									
3926	4.30	0.055	0.80	0.115	0.46	<0.005	0.065	0.29	4.7
<i>Sirius</i> 49	3.5	0.08	0.10	0.48	0.51	0.015	0.015	0.19	3.7

\* The analyses for the *Trial* and *Vergulde Draeck* cannon gave anomalously high carbon values because the metal was corroded.

† The carbon equivalent is defined by  $C_{eq} = C + 1/3(Si + P)$ . n.a. = values for these cannon were not calculated.

carronade. High levels of phosphorus and low levels of silicon are both associated with a low temperature of blast furnace operation<sup>15</sup>.

The *Rapid* cannon bears the cipher of G III R and so it is unmistakably an English cannon—the high nickel impurity is probably associated with a particular nickel mineral deposit that was coextracted with the iron ore. The only cannon with atypical composition is that of the *Fairy Queen* (1875); the 2.54% silicon content is very high and in a similar way the manganese level of 1.30% and 1.04% phosphorus are indicators of poor foundry practice or just a low quality ore. One of the apparent consequences of the composition is that the corroded zone of the cannon spalls away from the bulk of the object once it has been placed in alkaline solutions.

It was originally thought that drying out of the first *Fairy Queen* cannon prior to electrolysis treatment had caused the exfoliation. The second cannon of the matched pair was transported to the laboratory in a wet state and soaked in sodium hydroxide solutions without electrolysis and it too exfoliated. The small cannon have suffered from the high manganese content which favours formation of iron carbide (cementite) and the high phosphorus content would have made the metal brittle. The lower carbon content may have also contributed to the outer zone of the cannon having a different microstructure to the bulk of the material.

### Conclusion

The analysis of data associated with the desalination of corroded iron cannon during soaking and electrolysis in sodium hydroxide solutions, has provided an insight into the phenomena that control the rates of the process. From the interpretation of the washing and corrosion data obtained from twenty six cannon and ten wreck sites, it has been possible to develop a series of equations and relationships. The relationship  $t_n = k_n/d_g^2$  provides a method of calculating the number of days,  $t_n$ , it will take to reach the first and successive chloride concentration plateaus in the electrolysis solutions. The constants  $k_n$  have been experimentally determined and the annual depth of graphitisation,  $d_g$ , is the total depth of graphitisation,  $d$ , divided by the number of years of immersion. The total depth of corrosion is determined by drilling into the graphitised (corroded) metal until the drill-bit comes into contact with solid cast iron. The plateau constants and their relationship with  $d_g$  means that prediction of the treatment times is now possible.

The rate at which the chloride ions will be released is given by  $R = 3610 d_g^2$

– 0.110, where  $R$  is the normalised rate of chloride ion removal, expressed in terms of  $\text{mg} \cdot \text{hr}^{-1} \cdot \text{cm}^{-2}$ . The total number of kilograms of chloride ions to be extracted in the electrolysis treatment programme is given by  $\Sigma \text{Cl} = 0.0367d^2 + 2.61$ . Conservators can now use these relationships to provide a guide as to how long an electrolysis treatment will take. The data also provides a monitoring device of the extent to which the conservation programme has been completed. The normalised rate of chloride ion extraction can be used to calculate the sea water immersion time for cannon when the date of the shipwreck is unknown. This provides conservators and archaeologists with an unexpected dating method since the composition of cast iron cannon would normally only provide dating to within a century or two.

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### Note

1. All corrosion potentials are relative to the Normal Hydrogen Electrode (NHE) unless otherwise stated. The values have been calculated from the Ag/AgCl potentials recorded in the field.