Evaluation of Storage Solutions for Archaeological Iron

Charles G. Costain

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Evaluation of Storage Solutions for Archaeological Iron

Charles G. Costain

Canadian Conservation Institute, Department of Canadian Heritage, 1030 Innes Road, Ottawa ON K1A 0M5, Canada.

This study, carried out between 1983 and 1985, focusses on the evaluation of six solutions for their effectiveness as storage solutions for archaeological iron. These are aqueous solutions of sodium carbonate (1%), sodium hydroxide (1%), alkaline sulfite (0.5 M sodium hydroxide and 0.5 M sodium sulfite), and ethylenediamine (2%), seawater (synthetic), and deionized water. Groups of about 30 wrought iron nails from either a land or a marine site plus a pure iron coupon were stored for one year at room temperature in each of the six solutions; the dissolved oxygen and chloride ion concentrations in the solutions were monitored regularly. After one year in the storage solutions, 75% of the nails were treated (by ethylenediamine (5%, 60 °C), alkaline sulfite (60 °C), or hot washing) and the remaining 25% were assessed for susceptibility to corrosion by exposing their cross-section to open air at about 50% relative humidity. Alkaline sulfite and sodium hydroxide solutions were the most effective solutions for storing archaeological iron and are recommended. The sodium carbonate solution was less effective. The ethylenediamine solution, synthetic seawater, and deionized water are not recommended because of the probability of iron corrosion during storage.

Cette étude, menée de 1983 à 1985, porte sur l'évaluation de l'efficacité de six solutions aqueuses pour l'entreposage du fer archéologique. Des solutions de carbonate de sodium (1%), d'hydroxyde de sodium (1%), de sulfite alcalin (hydroxyde de sodium 0,5 M et sulfite de sodium 0,5 M), d'éthylènediamine (2%), l'eau de mer (synthétique) et l'eau déionisée ont été évaluées. Des groupes comprenant une trentaine de clous de fer forgé provenant d'un site marin ou d'un site terrestre et un coupon de fer pur ont été entreposés pendant un an à la température ambiante dans chacune des six solutions. Les concentrations d'oxygène dissous et d'ion chlorure ont été mesurées régulièrement. Après une année d'entreposage, 75% des clous ont été traités (éthylènediamine 5% à 60°C, sulfite alcalin à 60°C ou lavage à l'eau chaude), tandis que la tendance à corroder des autres clous a été évaluée en exposant à l'air des coupes préparées à partir de ces clous, à une humidité relative d'environ 50%. Les solutions de sulfite alcalin et d'hydroxyde de sodium étaient les plus efficaces pour l'entreposage du fer archéologique et sont recommandées. La solution de carbonate de sodium était moins efficace. Les solutions d'éthylèdiamine, l'eau de mer et l'eau déionisée ne sont pas recommandées à cause de la probabilité que la corrosion du fer ne soit accrue.

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Introduction

The problems associated with the excavation of iron from wet archaeological sites are widely recognized within the fields of conservation and archaeology. Iron that is allowed to dry out without undergoing some conservation treatment will usually corrode and disintegrate.¹⁻⁴ It is often impossible to carry out treatments to stabilize the iron in the field directly after excavation and artifacts are commonly stored in an aqueous solution until they can be transported to a laboratory for treatment.

This study, carried out between 1983 and 1985, evaluated the performance of a number of different iron storage solutions. Three qualities an iron storage solution should have are:

- 1. it should arrest corrosion during the storage period;
- 2. it should not interfere with subsequent conservation treatments;
- 3. it should minimize the time required for treatment of the artifact after storage.

Procedure

The six storage solutions that were evaluated in this study are listed in **Table I**. Sodium hydroxide and sodium carbonate

solutions have both been used extensively in the past for the storage of wet iron.⁵ Ethylenediamine⁶ and alkaline sulfite solutions⁷ are both used as conservation treatments for archaeological iron, but at elevated temperatures. It was decided to evaluate their performance as storage solutions when used at room temperature over a longer period of time. The other two solutions, deionized water and synthetic seawater,⁸ were chosen primarily for the purpose of comparison. It was not anticipated that they would provide very good protection for the artifacts. All of the solutions, except the deionized water and synthetic seawater, were strongly alkaline.

The artifacts used in this experiment were wrought iron nails from two sites: Red Bay and Gaspé Bay. The Red Bay site is a wet land site in Labrador, with artifacts dating to a sixteenth century Basque occupation. The Gaspé Bay site (off the east coast of the Gaspé region of Quebec) is an underwater shipwreck dating to the late seventeenth century. The artifacts from the Gaspé Bay site were initially in a large concretion and had to be removed prior to use in this experiment. The differences in the two groups of nails included their originating environment (land versus marine), age, duration of burial, and, although all wrought iron, probably small variations in composition. The two groups also differed in that the Red Bay artifacts were more heavily mineralized and were covered with a thick corrosion layer, while

| Solution | Remarks |
|---|---|
| Storage solutions at room temperature | |
| 1. 1% w/v sodium hydroxide | |
| 2. deionized water 2. 2% w/w ethylanodiamina | |
| A alkaline sulfite | - aqueous 0.5 M sodium hydroxide. 0.5 M sodium sulfite |
| 5. 1% w/v sodium carbonate | - 0.5 W sodium nyuroxide, 0.5 W sodium sume |
| 6. synthetic seawater | - ASTM Standard D 1141-75 ⁸ |
| Treatment solutions | |
| 1.5% v/v ethylenediamine | - aqueous, 60 °C |
| 2. alkaline sulfite | - 0.5 M sodium hydroxide, 0.5 M sodium sulfite, 60 °C |
| 3. distilled water | - 12 h cycle, 75 °C to room temperature |

the Gaspé Bay artifacts were mostly metallic iron with only a small amount of surface corrosion. As in all tests which make use of archaeological samples, the disparity in the samples leads to increased variability in the results.

In order to evaluate the performance of the storage solutions, it was necessary first to monitor the artifacts during the storage period and then to see how they responded to treatment after storage. The steps in the procedure are listed in **Table II** and an outline of the experimental design is shown in **Figure 1**.

The storage phase consisted of placing the nails from the two sites into their respective solutions and monitoring them for a period of one year. The nails from each site were divided up into seven groups, six of which were held in the storage solutions; the remaining group was frozen and used as a control group. There were about 30 nails per group stored together in their storage solution over the one-year period. Coupons of pure iron (99.98%, approximately 2 cm x 2.5 cm x 0.2 cm) were polished to remove any surface corrosion and then degreased using acetone. One coupon was included in each holding solution to act as a control. Monitoring of the solutions consisted of measuring the dissolved oxygen and chloride ion concentrations. The solutions were changed every three months. The weight of the pure iron coupons was monitored to evaluate the rate of corrosion.

Following the one year storage period, the nails from each solution and from the frozen control groups were further divided up into four subgroups. The nails from one of these subgroups were used for cross-section analysis and each of the other three subgroups were stabilized using one of the following treatments: 5% ethylenediamine at 60 °C as outlined by Argyropoulos et al.,6 alkaline sulfite at 60 °C following North and Pearson's procedure,⁷ or intensive washing in distilled water with the water temperature cycled between 75 °C and room temperature over 12 hours (see Table I). The chloride ion concentration of the treatment solutions was monitored regularly until a low chloride level was reached (see section on monitoring treatment solutions). Once low chloride levels had been reached, the nails treated by hot washing were dewatered in acetone and left to dry. Nails treated in ethylenediamine or alkaline sulfite solutions were hot washed until a neutral pH was reached before they were

| | | Steps | |
|-------------------|---|------------------------------------|---------------------------|
| | Iron in Storage Solution | Iron in Treatment Solution | Iron after Treatment |
| Time | 1 years | various (time until low chlorides) | 1 year after treatment |
| Number of samples | approx. 30 nails/group and 1 iron coupon | approx. 7 nails/sub-group | approx. 7 nails/sub-group |
| Monitor | - dissolved oxygen - dissolved chlorides - weight of coupon | - dissolved chlorides | - appearance |

Table II. Outline of Experimental Procedure.



Figure 1. Experimental design showing distribution of nails.

dewatered with acetone and left to dry. After drying, the nails were left at ambient laboratory conditions.

Experimental Conditions

Iron Storage Solutions

The storage solutions were made up using deionized water and reagent grade chemicals. Plastic pails were used as the storage containers; lids were placed on the pails, but they were not sealed. Approximately 6 L of solution were used for each group of 30-35 nails, which in total weighed in the range of 500 g.

Dissolved Oxygen Measurement

The concentration of dissolved oxygen in the storage solutions was monitored on a weekly basis using a YSI Model 54A Dissolved Oxygen Meter and probe. The solutions were stirred for one minute before the meter was turned on, and a reading was recorded once the meter had stabilized.

Monitoring of Chloride Concentration

A sample of 5 mL of solution was removed from the storage solution for analysis. The chloride content of the storage solutions was initially determined by adding a known excess of

silver nitrate solution to an acidified sample of the holding solution, thereby precipitating silver chloride. The amount of unreacted silver ion was then measured using atomic absorption spectrophotometry.⁹ Although this procedure was satisfactory, there is a large error in measuring the chloride concentration at lower chloride levels.

Later readings were taken using a modified Gran's Plot titration technique using a silver/sulfide specific ion electrode.¹⁰ This technique resulted in improved speed and accuracy for lower chloride readings. The same method was also used to monitor the chloride content of the ethylenediamine and alkaline sulfite treatment solutions.

Monitoring of the Pure Iron Coupons

The modern pure iron coupons were removed from the solutions at the end of each 3-month period when the solutions were being changed. They were rinsed with distilled water and then with acetone, allowed to dry, weighed, and then replaced in the fresh solution. The iron coupons were not brushed before weighing.

Cross-section Examination of Nails After Storage

Four nails were selected for cross-section examination from each storage solution. The nails were mounted in an epoxy resin and then using non-aqueous cutting fluids and lapping oils, were sectioned on a low-speed saw, then ground and polished, and finally rinsed in heptane. The sections were left exposed to ambient laboratory conditions at approximately 50% relative humidity for several weeks before microscopical examination. When corrosion did occur on the cross-sections, it was usually evident within a week of preparation.

Monitoring of Treatment Solutions

The ethylenediamine and alkaline sulfite treatment solutions were sampled on a weekly basis and the chloride level was determined using the Gran's Plot titration procedure described above. The solution was changed when the chloride concentration became constant over several weeks and the treatment was terminated when the solution contained less than 30 ppm chloride for six consecutive weeks.

The hot wash treatment was monitored on a daily basis using a qualitative silver nitrate test for chlorides.¹¹ The water was replaced whenever a positive result was obtained and the treatment was terminated when negative results were noted for two consecutive weeks.

Results

Dissolved Oxygen Content

The dissolved oxygen content of the solutions can be an important factor in predicting the effectiveness of a solution for protecting iron. If, as expected, the predominant cathodic reaction in the corrosion of iron objects is the reduction of



Figure 2. Dissolved oxygen content of the six experimental iron storage solutions.

film of corrosion products that formed on the surface of the solution which, in turn, may have sealed the solution from any contact with atmospheric oxygen.

Chloride Concentration

The presence of chlorides in the corrosion products promotes ongoing atmospheric corrosion of iron artifacts after treatment.¹⁴ Their removal is, therefore, desirable. If the removal of chlorides can be done during the storage period, it will result in subsequently shorter treatment time. The total amount of chlorides removed from the artifacts for each quarter of the storage year is shown in **Figure 3**. (Note that the synthetic seawater storage solution, which has a high chloride content, is not included in **Figure 3**.)

There are two clear trends that are evident from the data. First, the Gaspé

oxygen, a low dissolved oxygen content should result in a slow rate of corrosion.¹² Typical levels of dissolved oxygen in water at 20 °C range from 9.1 mg/L in pure water to 7.3 mg/L in seawater site. The

The dissolved oxygen content of the twelve storage solutions is shown in **Figure 2**. The weekly readings have been averaged for each 3 month period. The oxygen concentration of the

solutions appeared to reach a relatively constant value within a day of their preparation, although there was some variation in readings from week to week.

seawater.¹³

The only storage solution that gives consistently low dissolved oxygen readings for artifacts from both sites is the alkaline sulfite storage solution. This result had been anticipated as sodium sulfite is a strong reducing agent commonly used in industry for the reduction of oxygen in water systems.

Although the ethylenediamine solution used in the storage of the Gaspé Bay artifacts did show very low dissolved oxygen values for the initial three month period, the dissolved oxygen content was considerably higher for the following nine months. It is possible that this isolated low dissolved oxygen result was due to a



Figure 3. Concentration of chloride ions leached into iron storage solutions. The solutions were changed every three months.

Bay material contains more chlorides than the Red Bay artifacts; this is to be expected as the Gaspé Bay material is from a seawater site. The second observation is that, particularly for the Gaspé Bay artifacts, a large proportion of the chlorides that are removed from the artifact are leached out in the first three months.

It is not possible to directly compare the amounts of chloride



Figure 4. Cross-section with a corrosion rating of "not corroded." Black areas are voids.

removed by the various solutions as it is unlikely that the groups of artifacts contained equal amounts of chlorides to begin with. These results do indicate that the alkaline sulfite and sodium hydroxide solutions both removed large amounts of chloride from the Gaspé Bay and Red Bay artifacts while the deionized water removed very little. The ethylenediamine and sodium carbonate storage solutions removed large amounts of chloride from the Gaspé Bay nails, but seemed less effective in removing chlorides from the Red Bay artifacts.

Cross-section Examination

After one year in the storage solutions, four nails were removed from each of the storage solutions and cross-sectioned. If the artifacts are prone to corrosion, this will be observed on the sectioned surface after a few weeks at a relative humidity of 50%. Although a relatively small sampling of the groups was taken (4 nails out of about 30), it was felt sufficient to give an indication of the long-term stability of the artifacts.

The results of the examination are shown in **Table III**; a rating of "not corroded" means that no corrosion was observed, a rating of "slightly corroded" means that only a very small isolated spot of corrosion was observed, and a rating of "clearly corroded" was given to sections that showed a greater amount of corrosion. **Figures 4, 5**, and **6** illustrate the differences between the cross-sections. These figures also illustrate typical differences between the artifacts from the two sites; most of the nails from the Red Bay site have thick corrosion layers while the nails from the Gaspé Bay site mostly consist of bare metal.

These results correlate with those of the total chloride removal during storage; they show that the alkaline sulfite and sodium hydroxide storage solutions resulted in comparatively stable artifacts. The artifacts that had been stored in the sodium carbonate solution, deionized water, or synthetic seawater, or that

| Solution | Site | Number Not Corroded | Number Slightly* Corroded | Number Clearly Corroded |
|--------------------|-----------|---------------------|------------------------------|----------------------------|
| Sodium hydroxide | Red Bay | 2 | 2 | 0 |
| | Gaspé Bay | 4 | 0 | 0 |
| Deionized water | Red Bay | 0 | 0 | 4 |
| | Gaspé Bay | 2 | 0 | 2 |
| Ethylenediamine | Red Bay | 0 | 2 | 2 |
| | Gaspé Bay | 3 | 1 | 0 |
| Alkaline sulfite | Red Bay | 3 | 0 | 0 |
| | Gaspé Bay | 3 | 1 | 0 |
| Sodium carbonate | Red Bay | 0 | 0 | 4 |
| | Gaspé Bay | 1 | 1 | 2 |
| Synthetic seawater | Red Bay | 0 | 0 | 4 |
| | Gaspé Bay | 0 | 0 | 4 |
| Frozen control | Red Bay | 0 | 1 | 3 |
| | Gaspé Bay | 0 | 0 | 4 |

Table III. Results of the Examination of Cross-sections After Storage.

* Slightly = pieces with isolated spots of corrosion



Figure 5. Cross-section with a corrosion rating of "slightly corroded."



Figure 6. Cross-section with a corrosion rating of "corroded."

had been frozen showed a tendency to corrode. The nails from the Gaspé Bay site that were stored in the ethylenediamine solution appeared to be stable whereas those from the Red Bay site showed a tendency to corrode.

Rate of Corrosion of Modern Iron Coupons

Because of the corrosion layers on the artifacts, it was not possible to measure the corrosion rate of the iron nails either through monitoring their weight or the amount of iron in the solutions. Therefore, the weight of the pure iron coupons was monitored in order to determine whether or not iron metal was corroding in the storage solutions. It is understood that these results cannot be assumed to be directly applicable to actual artifacts; the coupons differ from the artifacts in that they are made of pure iron, are of modern manufacture, and have no



Figure 7. Rate of corrosion of iron control coupons in storage solutions.

corrosion products or concretions on their surface. However, if the iron coupon did corrode during the storage period this would indicate that the solution is detrimental to iron artifacts.

The weight of the iron coupons was recorded at the end of each three month period and the weight loss is shown in **Figure 7** as the rate of corrosion. No weight loss was detected with the iron coupons that were stored in the sodium hydroxide, alkaline sulfite, or sodium carbonate solutions. Both the deionized water and the synthetic seawater solutions, however, showed that the iron coupons were corroding in all four quarters of the storage year, whether they were stored with the Gaspé Bay or Red Bay artifacts. A published rate for the corrosion of steel in quiet seawater is 25 milligrams per square decimeter per day, or 0.25 milligrams per square centimetre per day.¹⁵ This is in the same range as the results obtained for the iron coupons.

The ethylenediamine solution showed different results for the iron coupon in the solution with the Red Bay artifacts than it did for the iron coupon with the Gaspé Bay samples. While the former coupon showed no corrosion, the latter corroded and lost weight through every three-month period of the storage year.

Conservation Treatment After Storage

All three conservation treatments (ethylenediamine, alkaline sulfite, and hot washing) were terminated when no further chloride was extracted into the treatment solutions. A short treatment time may indicate either that only very small amounts of chlorides remained in the artifacts after the storage period or that the treatment was not effective in removing the remaining chlorides.

The treatment times for the artifacts (as opposed to the storage time) are shown in **Figure 8**. Although there was considerable variation between the time required for the different conservation treatments of artifacts from any one storage solution, **Figure 8** shows that the artifacts stored in alkaline sulfite or sodium hydroxide solution required the shortest treatment time. The Gaspé Bay material that was stored in the ethylenediamine solution also only required short treatments while the Red Bay material stored in the ethylenediamine solution required considerably longer treatment. The material from the other storage solutions (deionized water, sodium carbonate solution, and synthetic seawater) as well as the frozen control group generally required longer treatment times.

It is quite apparent from **Figure 8** that there is a large discrepancy among the different treatments. The treatment time required for either ethylenediamine or alkaline sulfite treatments was usually quite similar within a group of artifacts whereas the time required for the hot wash treatment varied considerably in some cases. In fact, the hot wash method resulted in the shortest treatment time for all of the Red Bay artifacts which likely indicates that very little chloride was extracted. This result is consistent with previous studies on artifacts from Red Bay^{16, 17} and elsewhere,¹⁸ in which hot wash treatments were found to be considerably less effective for stabilization of artifacts than either the alkaline sulfite and/or ethylenediamine treatments.

The results for the time of ethylenediamine or alkaline sulfite treatments correlate well with the results of chloride removal and cross-section examination. The least time for treatment was required by artifacts that had been stored in the alkaline sulfite solution, followed closely by those stored in the sodium hydroxide solution. The Gaspé Bay artifacts stored in the



Figure 8. Time required for treatment of artifacts after one year in storage solutions.

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ethylenediamine solution also required only a short treatment, but the Red Bay artifacts stored in the same solution required considerably longer treatment.

It is interesting to look at the amount of chloride removed during the ethylenediamine and alkaline sulfite treatments (**Figure 9**) in relation to the actual time of treatments shown in **Figure 8**. Note that the results of the chloride removal from the hot wash treatment are not included in **Figure 9** as the presence of chloride in these solutions was monitored qualitatively using a silver nitrate test. **Figure 9** shows how little additional chloride was removed during the treatment phase after storage in the alkaline sulfite or sodium hydroxide solution. All of the other solutions had comparatively large amounts of chloride removed during the treatment phase; the only exception to this was the Gaspé Bay material that had been stored in the ethylenediamine solution, which also seemed to be chloride-free.

Appearance and Stability of the Artifacts After Treatment

The condition and appearance of the treated nails was reviewed a year after completion of the treatments. The primary purpose was to visually identify the unstable artifacts and to correlate this with the analytical data that had been recorded during the storage and treatment phases.

In general, the nails from the Gaspé Bay underwater site had no corrosion layers and the metal surface had a "stripped," stringy appearance because of the burial environment. This characteristic seemed to be accentuated for the nails that were stored or treated in the ethylenediamine solution. The nails that had been stored in the sodium hydroxide or the alkaline sulfite holding solution were generally stable regardless of subsequent treatment or treatment

> type. The nails that had been stored in the ethylenediamine holding solution and then treated were stable. There was some corrosion in the nails which were not treated after storage in the ethylenediamine solution (a portion of which was used for cross-section analysis). The appearance of these nails was generally not desirable as they were deeply etched or stripped. Of the treatment procedures, both the ethylenediamine and the alkaline sulfite treatments resulted in generally stable artifacts for all nails except for the control group (frozen, no holding solution). The hot wash treatment seemed to be marginally less effective.

> The nails from the Red Bay site generally had their thick corrosion layers retained, although this was variable. Again, the sodium hydroxide or the alkaline sulfite holding solution seemed to result in the most stable artifacts regardless of whether any

treatment was used following the storage period. Artifacts that had been placed in the ethylenediamine holding solution showed a tendency to corrode. Of the treatment processes, the nails treated using the alkaline sulfite were the most stable. The ethylenediamine treated artifacts were generally stable, but exhibited occasional failures. The hot wash process was not very effective for these artifacts; all groups showed corrosion except for those which had gone through the sodium hydroxide or alkaline sulfite holding solution.

Discussion

Much of the present study was carried out during the early 1980s and, although not published until now, the results are relevant because they specifically address the effectiveness of solutions for the storage of archaeological iron prior to treatment rather than the treatment of archaeological iron per se. The treatments (ethylenediamine, alkaline sulfite, hot washing) were evaluated in relation to the holding solutions and no attempt has been made to draw any conclusions as to the effectiveness of these as treatment solutions.

The results from this study indicate that the most effective storage solutions for archaeological iron are the alkaline sulfite or sodium hydroxide solutions. Since the effectiveness of these two solutions as treatment solutions has been demonstrated,^{2,18,19} it is not surprising that they would also be effective as storage solutions.

The alkaline sulfite solution has a very low dissolved oxygen content. This should result in minimal corrosion of metal during storage and prevent further oxidation of the existing corrosion products. The alkaline sulfite storage solution was effective at removing chlorides from the artifacts during the storage period;

1000 Chlorides Removed during Conservation Treatments (ppm) Red Bay Gaspé Gaspé Gaspe 800 Ethylenediamine Treatment Alkaline Sufite Treatment 600 Red Bay Red Bay Red Bary Red 400 Bay 200 Gaspe Red Red Gaspe Gasu Gaspé Bay Bay Û 1% Sodium Deionized 2% Alkaline 1% Sodium Synthetic Frozen Hydroxide Water Ethylenediamine Sulfite Carbonate Seawater Control

Figure 9. Chlorides removed during treatments (following 1 year of storage).

no additional chloride was removed during subsequent treatment. The cross-section examination of nails from this solution indicated that the artifacts were quite stable after storage. Observations of the stability of the artifacts following storage and treatment indicate that no additional treatment of the artifacts may be necessary following prolonged storage in these solutions. Work by Gilberg²⁰ indicates that a 0.05 M solution of sodium sulfite is effective for the storage of archaeological iron; the alkaline sulfite solution used here was made up of a solution of 0.5 M sodium sulfite and 0.5 M sodium hydroxide. It is quite possible that equally effective results could be obtained with a substantially lower concentration of both sodium sulfite and sodium hydroxide. Due to the caustic nature of the chemicals, as well as problems posed by chemical disposal, this would be worth investigating.

The sodium hydroxide solution showed very similar results in all categories with the exception of the dissolved oxygen concentration. The sodium hydroxide solution did not have a low dissolved oxygen content, but it does have inhibitive properties in the case of clean iron.²¹ As Turgoose¹² points out, this does not mean that there is no corrosion taking place beneath a corrosion layer. The sodium hydroxide solution did remove chloride effectively during the storage period. Subsequent conservation treatments resulted in the removal of very little additional chloride. The sample of nails that was examined using cross-section analysis and the observations of the long-term stability of the treated artifacts indicated that the artifacts were quite stable after a year of storage in this solution. As mentioned for alkaline sulfite, it might be worth investigating whether equally effective results could be obtained with a substantially lower concentration of sodium hydroxide such as a 0.04% solution, still alkaline at a pH of 12.

> The ethylenediamine storage solution gave quite different results for the artifacts from the two archaeological sites. One surprising result was the corrosion of the pure iron coupon in the storage solution containing the Gaspé Bay samples, but not in the solution containing artifacts from Red Bay. It was initially thought that the aggressive behaviour of the solution might be linked to the chloride concentration, but in the final six months of storage the chloride concentration in the Gaspé Bay solution was less than that of the Red Bay solution. The iron coupon that was with the Gaspé Bay artifacts corroded in all four three-month periods while the coupon with the Red Bay artifacts did not corrode at all. While the pure iron coupon does not reflect the behaviour of an artifact it does indicate that this solution can be damaging to iron objects. There have been cases in



the archaeology laboratory of the Canadian Conservation Institute where the edges of a wrought iron object have been attacked during storage in ethylenediamine. Stripping during ethylenediamine treatment has also been reported in the literature.²²

The amount of chloride removed during storage also differed for the artifacts from the two sites. Most of the chloride from the Gaspé Bay material appears to have been removed during the storage period while in some cases a substantial amount of chloride remained in the Red Bay artifacts after storage. This was removed during the subsequent conservation treatments. This result can be explained by the difference in the artifacts from the two sites; the Gaspé Bay material had very little corrosion product covering the metal while the Red Bay artifacts were encased in a sheath of compact corrosion products. This would make it more difficult for the chlorides to diffuse away from the metal into the solution in the case of the Red Bay artifacts. It seems, however, that the alkaline sulfite and sodium hydroxide solutions did achieve effective chloride removal from the Red Bay material during storage, in spite of the corrosion layer.

The sodium carbonate solution did not appear to be particularly effective for chloride removal during storage, especially for the Red Bay material. The sample that was examined after storage and before treatment showed poor stability at 50% relative humidity.

The deionized water and synthetic seawater solutions both performed poorly as storage solutions. The iron coupons indicate that corrosion could be continuing during storage, and neither solution was effective in removing chlorides from the artifacts.

Conclusions

This study indicates that the alkaline sulfite and sodium hydroxide storage solutions are both effective for storing iron artifacts. Although we cannot be certain that no corrosion was taking place during storage, there was no clear evidence of corrosion of artifacts or of modern iron coupons stored in these solutions. The solutions appear to be compatible with, and minimize the treatment time for conservation treatments that were carried out after storage.

The ethylenediamine solution shows some undesirable characteristics as a storage solution. Although it could not be established that the artifacts stored in this solution were corroding, the modern iron coupon in the solution did corrode. The stringy appearance of the Gaspé Bay artifacts indicates the possibility that corrosion was taking place on the artifacts as well. In addition to this, the Red Bay artifacts that had been stored in the ethylenediamine solution still contained chloride and required considerably longer treatment times than were necessary for similar artifacts that had been stored in the alkaline sulfite or sodium hydroxide solution.

The sodium carbonate solution was not effective in removing chlorides during the storage period. It did provide protection for the iron control coupons as it also passivates the metal surface. After a year of storage, however, additional chlorides were extracted during the conservation treatments, and the time required for treatment was, in most cases, similar to that required for the frozen control group.

The deionized water and synthetic seawater solutions are not suitable for iron storage. They do not provide a passivating environment for the iron. It is likely that corrosion is taking place during the storage period. In addition, they are not effective at removing chlorides from the artifacts and the treatment time required after storage is similar to that required for the control group.

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