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Iron Stain Removal from Archaeological Composite Artifacts made of Wood and Iron

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When some composite wood-iron artifacts from a marine archaeological site became stained by iron corrosion products during storage, a procedure had to be developed to remove the staining from the wood surface. Eight solutions were evaluated to determine how well they could remove rust stains from paper (a convenient form of cellulose). The solutions included a combination of ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA), oxalic acid, thioglycolic acid, sodium dithionite with and without a chelating agent (EDTA), poly(vinylpyrrolidone) (PVP), and phosphoric acid with and without PVP. The most effective of these, sodium dithionite plus EDTA, was then tested further. It was found that the dithionite solutions should not be heated or exposed to air; that other chelating agents can be used instead of EDTA, such as DTPA or the sodium salt of N,N-di(2-hydroxyethyl)glycine (DHEG); that the concentration of chelating agent is not critical; and that the results are similar whether the sodium dithionite and chelating agent are used in the same solution or used sequentially in separate solutions.

Une procédure a été développée pour éliminer des taches de la surface du bois, après que certains objets composites bois-fer provenant d'un site archéologique marin aient été tachés par des produits de corrosion du fer pendant leur entreposage. Huit solutions ont été évaluées afin de déterminer leur efficacité à éliminer des taches de rouille sur du papier (une forme pratique de cellulose). Ces solutions comprenaient une combinaison d'acide éthylènediaminetétraacétique (EDTA) et d'acide diéthylènetriaminepentaacétique (DTPA), l'acide oxalique, l'acide thioglycolique, le dithionite de sodium avec ou sans un agent chélatant (EDTA), le poly(vinyl pyrrolidone) (PVP) et l'acide phosphorique avec ou sans PVP. La solution la plus efficace, le dithionite de sodium avec EDTA, a ensuite été testée de manière plus approfondie. Ce travail a montré que les solutions de dithionite ne devraient pas être chauffées ni exposées à l'air; que d'autres agents chélatants peuvent être utilisés à la place de l'EDTA, comme du DTPA ou le sel de sodium de la N,N-di(2-hydroxyéthyl)glycine (DHEG); que la concentration d'agent chélatant n'est pas critique; et que les résultats sont similaires que le dithionite de sodium et l'agent chélatant soient présents dans la même solution ou bien utilisés en séquence dans des solutions distinctes.

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Introduction

The research presented here was motivated by a problem that was noted in 1992 during treatment of composite wood-iron objects at the Ottawa laboratories of Parks Canada.[1] The wood in some of the objects was found to be stained orange-brown with iron corrosion products after a traditional treatment using polyethylene glycol (PEG) and vacuum freeze-drying, so steps had to be added to the treatment to reduce the stain.

Many of the composite objects with iron-stained wood came from the shipwreck site of the *Machault* in the Restigouche estuary, which separates the provinces of Quebec and New Brunswick, Canada.[2] The *Machault* was an 18th-century frigate; it sank in 1760 and was excavated between 1969 and 1972 after being buried for 200 years under the riverbed in brackish water. The composite objects were stored in deoxygenated water for some years before treatment. During storage, the objects were removed from the tanks once a year, cleaned with brushes and flowing water, and replaced in the tanks. Although the storage tanks were deoxygenated with flowing nitrogen, the objects gradually became coated with flocculent orange-brown rust after each year of storage, and some orange-brown staining penetrated the wood surface.

In the original treatment, the composite objects were removed from wet storage, soaked in solutions of PEG and Hostacor KS1, and then vacuum freeze-dried. The soaking in PEG took place in two steps: first, PEG 400 (20% v/v), then PEG 400 (20% v/v) plus PEG 3350 (5% w/v or 10% w/v). The PEG concentrations were calculated using the PEGcon computer program.[3] Hostacor KS1 (1% v/v) was added to these PEG solutions to inhibit iron corrosion during treatment.[4] (Note that Hostacor KS1 is no longer available and has been replaced by Hostacor IT.[5]) Although the wood had been thoroughly cleaned before impregnation (with brushes, dental tools and cavitron), and although PEG treatments do remove some iron ions,[6] orange-brown stains were visible once the treated wood had dried. It was thought that these stains had probably formed before treatment, during storage.

The orange-brown rust stains (probably the two iron oxyhydroxides, lepidocrocite, γ-FeOOH, and/or goethite, α-FeOOH, and possibly also magnetite, Fe_3O_4) had coloured the wood surface. The archaeologists asked the conservators to modify the treatment to eliminate the staining. The goal of the work presented here was to find a treatment step that could be used on the waterlogged artifacts prior to the PEG/Hostacor treatment, to remove any rust stains formed during storage. Note that this treatment step was developed to remove surface staining only, not to remove iron ions that might have penetrated deep into the wood while the shipwreck was underwater. There was no evidence of any problems associated with deep iron contamination, which can catalyze degradation of cellulose and destroy contaminated wood.[7] No such degradation had been observed on wood or iron-wood composites from the site after these objects had been treated and subsequently stored at 50 ± 5% relative humidity. Iron catalyzed degradation of wood cellulose might be an issue in the long term but the proposed testing was intended only to address surface appearance issues.

Various solutions were tested for removing iron stains, using paper as a simple substitute for wood, and the combination of a chelating agent (ethylenediaminetetraacetic acid, EDTA) and a reducing agent (sodium dithionite) was identified as the best of the solutions tested. This paper presents the results of these tests.

Testing Strategy

Testing for stain removal was completed in two parts. In the first part, eight solutions were tested for their effectiveness in removing iron staining from paper. The eight test solutions were chosen from earlier studies on iron stain removal from paper[8] and from textiles.[9] These solutions were tested on two types of stained paper: chemically-stained paper prepared by soaking in an iron-containing solution, and residue-stained paper that had been coated with the iron corrosion products from artifacts. Samples of both types of paper were treated in each of the solutions, and reflectance was measured before and after treatment. Based on the difference in reflectance, the most effective solution was identified to be a mixture of sodium dithionite and a chelating agent (EDTA).

In the second part, further testing was done to examine three aspects of treatment with this solution. First, tests were done at different temperatures, with or without exposure to air, to check the stability of the solution. Then different concentrations and different chelating agents were compared, to see whether either the concentration or the type of chelating agent was critical. Finally, the two components in the solution (sodium dithionite and the chelating agent) were tested sequentially, to see if a sequential treatment offered any improvement over a treatment with the two components in the same solution.

Preparation of Paper Samples

These experiments were designed to test how effectively test solutions removed iron stains from cellulose, the main constituent in wood. White blotting paper was chosen as a convenient form of cellulose and was intentionally stained with iron corrosion products. Two sets of iron-stained samples were prepared. One set, referred to as "chemically-stained," was made with a procedure adapted from Hawley et al.[8] Sheets of blotting paper were soaked in a 5% w/v solution of iron(II) sulfate for five minutes and air dried. Then the sheets were placed in a 10% v/v solution of ammonium hydroxide for 10 minutes and air dried overnight. After this procedure, the paper was uniformly covered with light orange-brown stain (probably lepidocrocite, although this was not confirmed by analysis). A second set of samples, referred to as "residue-stained," was made by brushing sheets of blotting paper with several coats of orange-brown residue from the wet wood surface of the *Machault* composite artifacts. The orange-brown deposit presumably formed when the iron in the artifacts corroded, producing iron corrosion products that precipitated from solution. Several coats of corrosion product taken directly from the wood surface were applied by brush to one side of the blotting paper, with different layers applied in different directions to produce a uniform orange-brown coating. The sheets were left to air dry overnight. The coating is likely a mixture of lepidocrocite, goethite and magnetite, although this was not confirmed by analysis. Samples measuring 4 x 5 cm were cut from the sheets: 50 samples were cut from the chemically-stained sheets and 54 samples were cut from the residue-stained sheets. Forty samples from each set were used in the test solutions in Part 1. For Part 2, more residue-stained sheets were prepared using the same staining procedure.

Part 1: Effectiveness of Eight Solutions

Procedure

The eight solutions were prepared using distilled water and chemicals available in the conservation laboratories at Parks Canada in Ottawa. The chemicals used were technical grade (typically used for treating objects) rather than the more expensive high-purity analytical grade. The eight solutions and their concentrations are listed in **Table I**. To prepare solutions of EDTA and EDTA plus diethylenetriaminepentaacetic acid (DTPA), it was necessary to add sodium hydroxide to dissolve the crystals of these two compounds. **Table I** also lists the pH of freshly prepared solutions, measured with a Hanna HI 8417 electronic pH meter. Solutions were prepared and used within an hour.

The reflectance at 457 nm was measured to assess the brightness of the samples before treatment, using the same wavelength as Hawley et al.[8] The spectrometer was a Perkin-Elmer/Hitachi 200 UV/Vis spectrometer with a model 200-0530 integrating sphere attachment with a spot size of 18 mm. The results were recorded as a percent reflectance (%R). For each of the chemically-stained paper samples, two %R readings were made, one on each side of the paper. For the residue-stained paper samples, only one %R reading was recorded, since only one side had been stained.

Test solutions were placed in 16 polyethylene beakers, so that each of the eight solutions could be tested with each stain type. Five paper samples were suspended in the solution in each beaker with plastic hemostatic clamps. The beakers were large enough to hold five suspended samples and enough solution was added to cover the samples. The beakers were not sealed. Samples were removed at different times (5, 10, 20, 40 and 60 minutes). Once removed, the paper was rinsed in warm water (~30℃) for 30 minutes and then dried overnight. The dried paper samples were immersed in 10% v/v ammonium hydroxide for 10 minutes to precipitate residual iron salts to a visible form, then rinsed for 20 minutes in warm water (~30℃) and air dried.

Once samples were dry, the reflectance was measured again to assess the change in brightness. The solutions were then ranked as to how effective they were at removing the iron stains from the two different kinds of stained paper.

Table I. Eight Solutions Tested for Effectiveness at Removing Iron Stains From Paper.

Chemical Name or Abbreviation	Formula	Concentration	pH
Ethylenediaminetetraacetic acid (EDTA) + Diethylenetriaminepentaacetic acid (DTPA)	$C_{10}H_{16}N_2O_8$ $C_{14}H_{23}N_3O_{10}$	1% w/v 0.5% w/v	9.2
Oxalic acid	$C_2H_2O_4$	2% w/v	1.3
Phosphoric acid	H_3PO_4	1% v/v	1.7
Phosphoric acid + Poly(vinylpyrrolidone) (PVP)	H_3PO_4 $(C_6H_9NO)_n$	1% v/v 1% w/v	1.9
Poly(vinylpyrrolidone) (PVP)	$(C_6H_9NO)_n$	1% w/v	4.1
Sodium dithionite	$Na_2S_2O_4$	10% w/v	4.3
Sodium dithionite + Ethylenediaminetetraacetic acid (EDTA)	$Na_2S_2O_4$ $C_{10}H_{16}N_2O_8$	10% w/v 1% w/v	5.1
Thioglycolic acid	$C_2H_4O_2S$	20% w/v	1.7

Results for Chemically-stained Paper

Based on 100 reflectance measurements, one on each side of the 50 chemically-stained samples cut from stained sheets prior to testing, the average %R and standard deviation for side one was 13.8 ± 1.3, and for the other side, 15.4 ± 2.0. The small standard deviations demonstrate the relative uniformity of the staining of the set of paper samples before treatment. **Table II** gives the change in percent reflectance (%R) for samples of chemically-stained paper immersed for one hour in one of the eight test solutions, listed in order from most effective at the top to least effective at the bottom. The higher the change in %R, the lighter the colour of the samples was after treatment and the greater the amount of stain removed. Since only two measurements were taken for each sample (one for each side), one half of the range is given along with the average as an indication of the spread of the results. (The one negative result indicates that the paper was darker after immersion than before, although this difference is so small, it is not significant.) The first four test solutions listed were effective at removing the iron stain on the chemically-stained paper; the other four were not effective. Thioglycolic acid worked faster than the other treatments; after 10 minutes, the shortest treatment time, the change in %R was 60 (rising eventually to 67), whereas for the other treatments, %R increased more slowly with immersion time.

Results for Residue-stained Paper

Based on reflectance measurements made on the 54 residue-stained samples cut from the stained sheets prior to testing, the

Table II. Change in Percent Reflectance (%R) for Chemically-stained Paper Immersed for One Hour in the Eight Solutions. Half the Range is Given in Brackets.

Test Solution	Change in %R	Final Appearance
Thioglycolic acid (20% w/v)	67 (1)	white
Sodium dithionite (10% w/v) + EDTA (1% w/v)	57 (11)	mostly white, small areas of light orange-brown
Sodium dithionite (10% w/v)	54 (3)	mostly white, small areas of light orange-brown
Oxalic acid (2% w/v)	44 (0)	light orange-brown
Phosphoric acid (1% v/v)	15 (2)	light orange-brown
Phosphoric acid (1% v/v) + PVP (1% w/v)	3.4 (0.7)	orange-brown
EDTA (1% w/v) + DTPA (0.5% w/v)	0.4 (0.0)	orange-brown
PVP (1% w/v)	-0.4 (0.0)	orange-brown

Table III. Change in Percent Reflectance (%R) for Residue-stained Paper Immersed for One Hour in the Eight Solutions.

Test Solution	Change in %R	Final Appearance
Sodium dithionite (10% w/v) + EDTA (1% w/v)	48	white with black streaks
Sodium dithionite (10% w/v)	28	white with black streaks
Thioglycolic acid (20% w/v)	6.5	light orange-brown
Oxalic acid (2% w/v)	1.5	light orange-brown
Phosphoric acid (1% v/v) + PVP (1% w/v)	0.6	orange-brown
PVP (1% w/v)	0.4	orange-brown
Phosphoric acid (1% v/v)	0.2	orange-brown
EDTA (1% w/v) + DTPA (0.5% w/v)	0.2	orange-brown

average %R was 4.3 ± 0.2. The small value of %R is due to the dark orange-brown sample colour; the small standard deviation shows the relative uniformity of the stain before treatment. **Table III** gives the change in %R for samples of residue-stained paper immersed for one hour in one of the eight test solutions, listed in order of most effective to least effective. Only one %R measurement was recorded for each sample, so no ranges are given. The two test solutions containing sodium dithionite, listed at the top of **Table III**, were the most effective at removing the iron stain from the residue-stained paper. The black residue observed on papers from these two solutions could be black magnetite that the dithionite did not remove from the corrosion products or iron sulfides formed by reaction with dithionite decomposition products. For thioglycolic acid, %R changed by more than 5 after just 5 minutes of treatment and was roughly independent of time for longer treatments, whereas for the other treatments %R increased with immersion time up to the longest time, one hour.

Comparison of Results

For a given solution, the changes in %R were smaller for the residue-stained papers than for the chemically-stained papers. There could be several reasons for this. First, there was a larger mass of iron corrosion products on the residue-stained paper, given the initial darker orange-brown colour. Second, the stain on the chemically-stained paper was probably a single compound (likely lepidocrocite), whereas the corrosion products on the residue-stained paper were a mixture of compounds of varying solubility. Finally, iron compounds on the residue-stained paper were presumably more crystalline, having formed by slow oxidation processes during storage in water, whereas the iron compounds formed on the chemically-stained paper were probably relatively amorphous particles of smaller size, having formed quickly by precipitation from solution at room temperature. Amorphous forms of iron oxides dissolve more readily than crystalline forms,[10,11] and smaller particles of a given iron oxide have a higher solubility than larger particles.[12] This is largely a reflection of the relative surface areas of the minerals.

Table IV summarizes the results from **Tables II** and **III**. It gives the results of each test, normalized so that the strongest response in each test is 100 and the least is 0. The results are ranked according to highest combined response for the two types of stains. The ideal solution would have a score of 100 for both the chemical stain and the residue stain. The best performer by this ranking method, dithionite with EDTA, gave the largest reflectance change (averaged over the two types of stain).

The results suggest that the best solution of the eight tested to remove iron staining is 10% w/v sodium dithionite plus a chelating agent, here 1% w/v EDTA. This conclusion is based on the amount of stain removed. Sodium dithionite plus EDTA was

Table IV. Summary of the Effectiveness of Eight Solutions at Removing Iron Stains from Paper.

	Normalized Change* in %R	
Solution	**Chemical Stain**	**Residue Stain**
Dithionite + EDTA	85	100
Dithionite	81	58
Thioglycolic acid	100	14
Oxalic acid	65	3
Phosphoric acid	23	0
Phosphoric acid + PVP	5	1
EDTA+ DTPA	1	0
PVP	-1	1

*For the chemical stain, 100 corresponds to a reflectance change of 67; for the residue stain, 100 corresponds to a reflectance change of 48.

the second most effective solution in removing the chemical stain from paper, and it was by far the most effective in removing the stain from the residue-stained paper. It was decided to study sodium dithionite plus a chelating agent in more detail and to compare different chelating agents.

Part 2: Effectiveness of Sodium Dithionite and Chelating Agents

After the results from the survey of eight test solutions were reviewed, experiments were designed to study the effectiveness of solutions of 10% w/v sodium dithionite and several chelating agents in removing iron stains from blotting paper. Three experiments were carried out to determine the effects of air and temperature, chelate type and concentration, and sequential application of dithionite and chelate. This work was not intended to find an optimal concentration of dithionite.

General Procedures

The test papers were cut from sheets of residue-stained blotting paper, prepared using the same procedure as in the initial survey of test solutions. (The chemically-stained paper was not used in this part.) The samples were typically rectangular (3 cm x 3.5 cm) or square (3 cm x 3 cm).

After immersion in a test solution, each paper sample was rinsed in distilled water for a minimum of one hour before being air dried. In the sequential tests, the rinsing was done only after the second solution. Initially the procedure did not include the rinse step, but without it the samples from Day 1 in experiments on the effects of temperature and air changed colour from white to yellow by the next day. This demonstrated the importance of rinsing and the mechanism of release of iron(III) stains – the dithionite reduced the Fe(III) to Fe(II), which was subsequently oxidized on the surface of the paper because the Fe(II) had not been removed by rinsing. These first samples were then immersed in distilled water and dried, and all subsequent samples were rinsed before drying.

Three chelating agents were studied, as summarized in **Table V**. The tetrasodium salt of EDTA was technical grade, as was typically used in treating objects in the ceramic conservation laboratory of Parks Canada. The other two were sold under brand names: Na_5DTPA, sold as a 41% w/w solution called CHEL 41 with a pH listed as 13.3, from Ciba Geigy; and the sodium salt of N,N-di(2-hydroxyethyl)glycine (DHEG), sold as a solid called Versene Fe-3 Flake by the Dow Chemical Company and Fisher Scientific.[13] Fresh solutions were prepared at the start of each experiment and used for the duration of the experiment; experiments ranged from one to four days. The pH of the solutions was measured with a Hanna HI 8417 electronic pH meter.

In test solutions where exposure to air was minimized, 300 mL Fleaker beakers were filled to capacity with the test solution, a blotting paper sample was added, and then the top was plugged with a rubber stopper, which forced out some solution and eliminated any air space. Each solution was exposed to air for a short time whenever a paper sample was removed and replaced with another one. In those test solutions where air was allowed to enter continuously, an 800 mL plastic disposable beaker was half-filled with solution, a paper sample was added, and then the beaker was covered with a lid pierced with a pipette to allow air to enter and to limit evaporation. The experiments were carried out at room temperature (approximately 22°C) except for one set of solutions in the experiments on the effects of temperature and air, where some of the solutions were heated to 35-44°C in a shallow water bath.

Sodium dithionite/chelating agent combinations were tested either in a single solution (with the paper sample immersed in a mixture of sodium dithionite and a chelating agent), or sequentially (with the paper sample immersed first in a solution of sodium dithionite and then in a solution of a chelating agent). The solutions were tested by placing a series of iron-stained blotting paper samples in them, one piece at a time, starting with the shortest immersion time and finishing with the longest. After each immersion time, the sample was removed from the solution and replaced with a new sample, which was then left immersed for the next specified time. Because the solution was not refreshed between samples, some solutions became less effective on later samples, as can be seen in the results below. This approach was chosen because it was easier to immerse one sample at a time with the limited equipment available and maintain a relatively oxygen-free environment. For each day of each experiment, the dry paper samples were mounted together on a sheet of poster board and photographed.

Effects of Temperature and Air

Procedure

This experiment was designed to study the effect of temperature and the presence or absence of air on the ability of two mixtures to remove iron staining. One mixture contained 10% w/v sodium dithionite and 2% v/v CHEL 41 (1.1% w/v Na_5DTPA, pH ~ 5). The other mixture contained 10% w/v sodium dithionite and 2% w/v Versene Fe-3 Flake (pH ~ 5). The solutions were tested open to the air or sealed from the air, at room temperature (22°C) or heated (35-44°C). Tests were done on three consecutive days.

Table V. Three Chelating Agents Tested with Sodium Dithionite.

Symbol or Commercial Name	Chemical Name
Na_4EDTA*	Ethylenediaminetetraacetic acid, tetrasodium salt
CHEL 41 (41% w/w Na_5DTPA in water)**	Diethylenetriaminepentaacetic acid, pentasodium salt
Versene Fe-3 Flake (NaDHEG)	N,N-di(2-hydroxyethyl)glycine, sodium salt

*Probably the dihydrate form $Na_4EDTA \cdot 2H_2O$.
**Although CHEL 41 is no longer available, a similar solution is available from Dow Chemical (Versenex 80) or from BASF (Trilon C Liquid).

During this experimental work, solutions were not refreshed between samples or from one day to the next. One sample at a time was immersed for 30, 60, 75 and 90 minutes on Day 1, and for 60, 90, 120 and 150 on Days 2 and 3. The sample was removed from the solution and replaced with a new sample after each immersion time.

Results

On the first day, solutions not exposed to air remained colourless but those exposed to air gradually turned a light yellow or orange-brown. Over the three days of testing, the solutions that had minimum exposure to air remained colourless. Six days after the solutions had been prepared, the solutions not exposed to air and kept at room temperature remained colourless but those that had been heated had turned orange-brown.

Figure 1 shows the samples from Day 1. Note that the solutions were not refreshed between samples, so the samples with longer treatment times were being treated in solutions that had had more time to degrade and which contained varying amounts of iron ions from samples previously extracted. In all the solutions exposed to air, the samples treated for 90 minutes were more stained than those treated for 60 minutes, indicating that the solutions had degraded noticeably by the time the last sample was being treated.

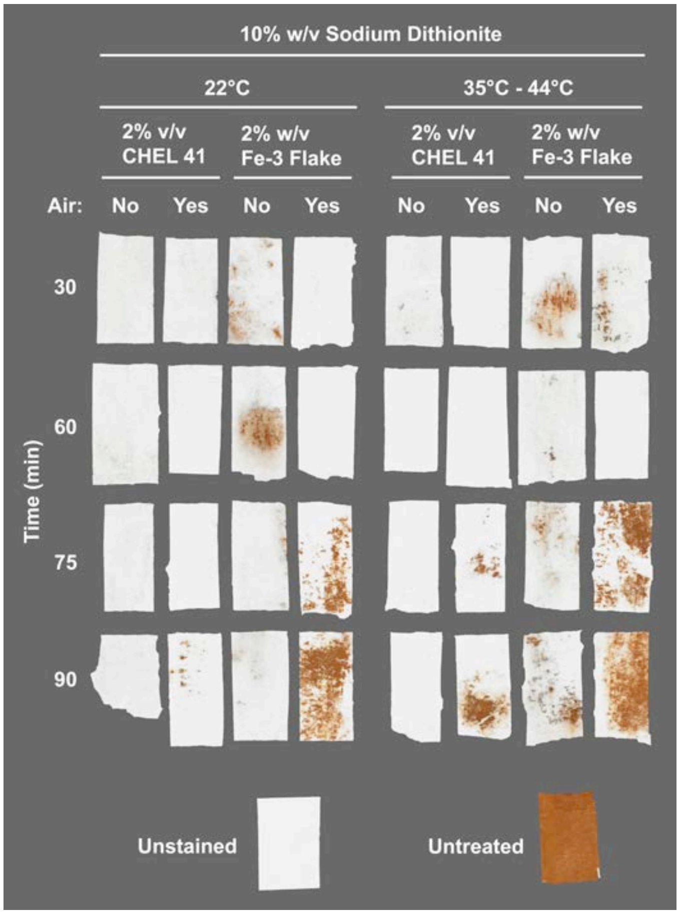

Figure 1. Samples from Day 1 testing of the effects of temperature and air. Times (left column) are in minutes. Solutions were 10% w/v dithionite plus a chelating agent, either 2% v/v CHEL 41 or 2% w/v Versene Fe-3 Flake. Samples were held at room temperature (22°C) or heated (35-44°C). Some samples were exposed to air (Yes) and others were not (No). Control samples are shown at the bottom.

By the second day, solutions exposed to air could not remove all the orange-brown stain from samples even for treatment times of 150 minutes, whether they were heated or not. The solutions with minimum exposure to air remained reasonably effective on the second day, although some grey remained on samples treated for 60 minutes or less. By the third day none of the heated solutions could remove the orange-brown stains; the only solutions that were effective by the third day were those that had been kept at room temperature with minimum exposure to air.

The results of this experiment confirm that sodium dithionite solutions must be stored sealed from the air and used as soon as possible after opening. It appears from **Figure 1** that solutions of sodium dithionite and CHEL 41 removed stains somewhat faster than solutions of sodium dithionite and Versene Fe-3 Flake, although the difference might not be significant in the treatment of iron stains on archaeological wood. The dithionite/chelate solutions with minimum exposure to air remained effective longer than solutions readily exposed to air. Moreover, solutions kept at room temperature remained effective longer than solutions heated to 35-44°C. In general, solutions exposed to air or heated remained effective only for a few hours. Even solutions not heated and not exposed to air were somewhat less effective by the second day. These results indicate that to maximize effectiveness sodium dithionite solutions used to treat objects should be made fresh, used as soon as possible and kept from air and heat.

Different Chelating Agents and Different Concentrations

Procedure

This experiment was designed to study the effect of varying the concentration of three different chelating agents. Six solutions were tested. Each solution contained 10% w/v sodium dithionite and one of three chelating agents, with each chelating agent tested at two different concentrations. The experiment was done with stoppered beakers, so exposure to air was minimized.

For Test 1, the pH of the solutions was not adjusted, whereas for Test 2, the pH was adjusted with acetic acid to pH = 5.0 before treatment. This value was chosen to reduce the pH by about 1 pH unit, to see if slightly more acid conditions would dissolve more iron stain but not to reduce the pH so much that wood might be damaged. Although both tests were carried out over more than one day, the solutions were noticeably less effective after the first day, and only the results from the first day are reported below.

Table VI lists the six solutions tested and the initial pH for Test 1 and Test 2. No significant change in pH of these solutions was noted over the course of these experiments.

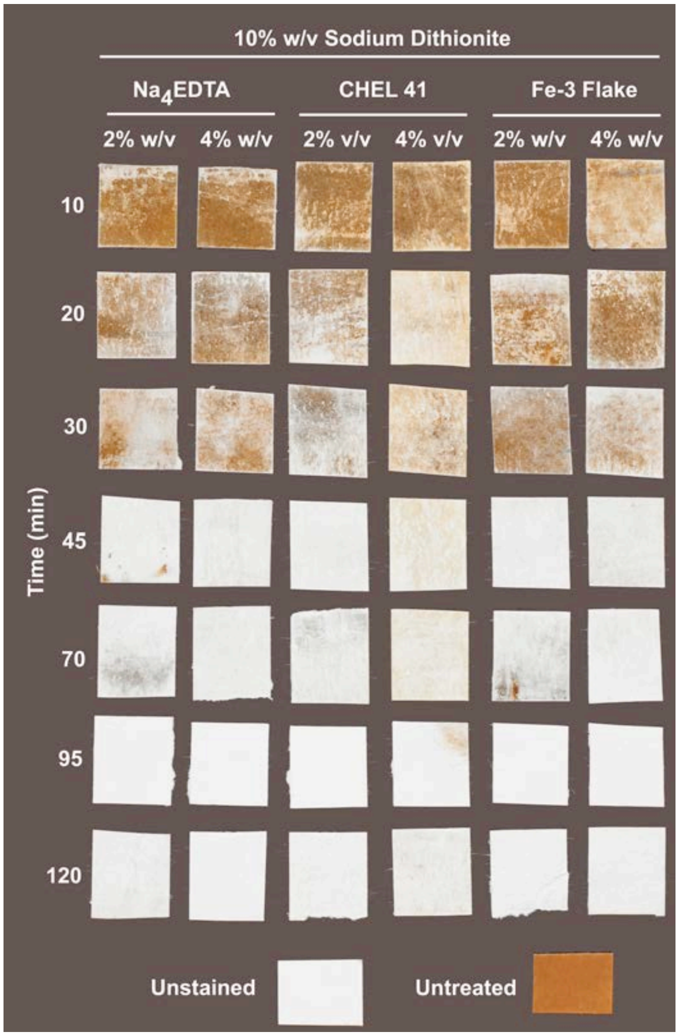

Figure 2. Test 1: Samples treated with 10% w/v sodium dithionite with the three different chelating agents Na_4EDTA, CHEL 41, or Versene Fe-3 Flake at two different concentrations, starting at an initial pH of 5.8-6.2. Times (left column) are in minutes. Samples were held at room temperature and kept from contact with the air. Control samples are shown at the bottom.

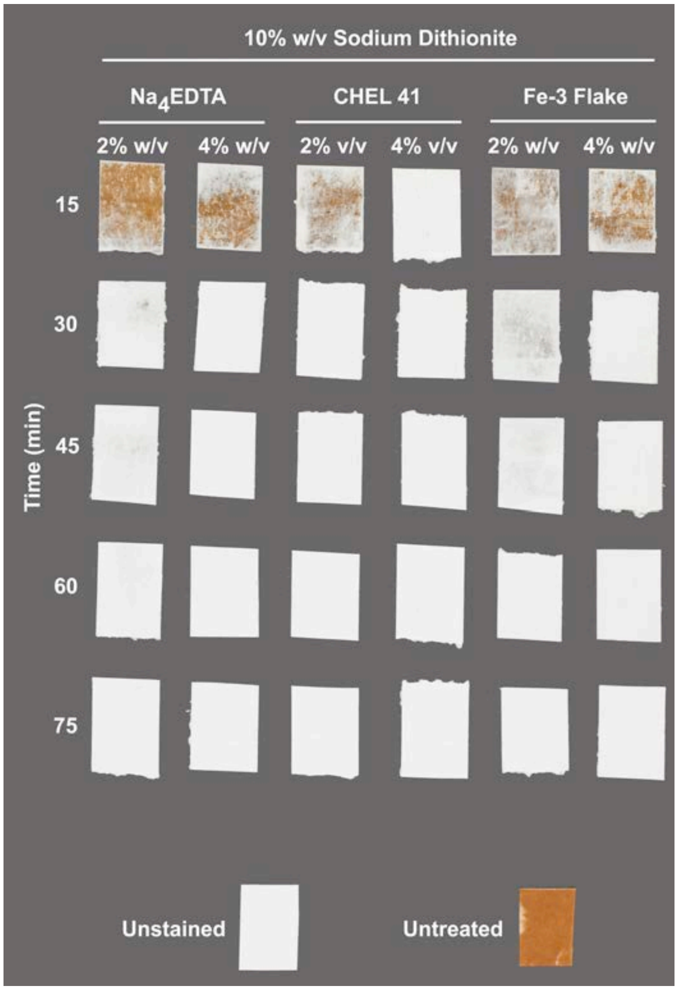

Figure 3. Test 2: Conditions as in **Figure 2**, except initial pH adjusted to 5.0.

Results

The results are shown in **Figure 2** (Test 1) and **Figure 3** (Test 2). There was in almost all cases no significant difference between 2% or 4% solutions in a given test. In addition, the concentration of the chelating agent or the type of chelating agent had little effect. All solutions eventually removed the iron stains, taking about 45 minutes without adjustment of pH (Test 1), or about 30 minutes with pH reduced to 5.0 with acetic acid (Test 2). The results suggest that if a wooden object cannot be treated in an acidic solution, a higher pH solution can be used with a slightly longer treatment time.

Table VI. Initial pH of Six Solutions of Sodium Dithionite with Different Chelating Agents at Different Concentrations.

	10% w/v $Na_2S_2O_4$ + Na_4EDTA		**10% w/v $Na_2S_2O_4$ + CHEL 41**		**10% w/v $Na_2S_2O_4$ + Versene Fe-3 Flake**	
	2% w/v	**4% w/v**	**2% v/v**	**4% v/v**	**2% w/v**	**4% w/v**
Test 1 (initial pH not adjusted)	5.9	6.2	5.9	6.2	5.8	6.1
Test 2 (initial pH adjusted with acetic acid)	5.0	5.0	5.0	5.0	5.0	5.0

Separate Solutions for Dithionite and Chelating Agent

Procedure

This experiment was designed to study the effectiveness of exposing the stained paper samples to the dithionite solution first, followed by a chelating agent solution, instead of exposing the samples to both chemicals at the same time. The experiment was done with stoppered beakers, so exposure to air was minimized. The stained paper samples were first immersed in a solution of 10% w/v sodium dithionite, then transferred to a second solution, either distilled water or a solution containing one of the chelating agents. The three chelating agent solutions were 2% w/v Na_4EDTA, 2% v/v CHEL 41, or 2% w/v Versene Fe-3 Flake. **Table VII** gives the concentration and initial pH of the solutions.

Table VII. Concentration and pH of Solutions Used to Test the Effectiveness of Using Dithionite Solution Followed by a Chelating Agent Solution.

Solution 1		Solution 2	
Concentration	**pH**	**Concentration**	**pH**
10% w/v $Na_2S_2O_4$	4.5	distilled water	6.4
10% w/v $Na_2S_2O_4$	4.5	2% w/v Na_4EDTA	11.0
10% w/v $Na_2S_2O_4$	4.5	2% v/v CHEL 41	9.1
10% w/v $Na_2S_2O_4$	4.5	2% w/v Versene Fe-3 Flake	10.7

Results

The results from this experiment are shown in **Figure 4**. After treatment and drying, most of the blotting papers had a black residue; the residue was darkest on the papers where no chelating agent was used in the second solution. In fact, the chelating agents seemed to have little effect aside from removing some of this black residue. Most of the orange-brown rust stain had disappeared from all of the papers after 15 minutes of immersion in dithionite solution. Longer immersion in dithionite (30-45 minutes) removed the remaining orange-brown stain. Most of the iron stain was removed by the dithionite solution, which was used first. The subsequent treatment in the chelating agent reduced the dark background colour on the paper observed after rinsing and drying. This background colour was most apparent on paper that was only rinsed in distilled water (i.e., not immersed in a chelating agent solution). Separate solutions of sodium dithionite and chelating agent gave similar results to those for a single solution with sodium dithionite and chelating agent combined.

Discussion

For a rust stain of iron oxide or oxyhydroxide to dissolve, the iron ions from the stain must get into solution and stay there. In other words, an effective treatment to remove iron stains must do two things: weaken the iron-oxygen bonds at the surface of rust particles in the stain and increase the solubility of iron ions in the solution. Treatments can do these things in one or more of the following three ways.[14] (1) They can increase the acidity; iron ions are more soluble in acid solutions than in neutral or basic solutions. Moreover, the H^+ ions in an acid adsorb on the surface of the stain particle and weaken the iron-oxygen bonds. (2) Treatments can add molecules such as chelating agents that attach to the iron ions on the surface and in solution. Chelated iron – iron with a chelating agent attached – is more soluble than unchelated iron.[12] (3) Treatments can reduce the iron ions from Fe(III) to Fe(II) on the surface and in solution. Fe(II) compounds are more soluble in water than Fe(III) compounds.

The three approaches can be combined to enhance the effects further. For example, Zinder et al.[15] found that goethite dissolved faster in a combination of oxalic acid (a chelating agent) and ascorbic acid (a reducing agent) than in either acid alone. (Oxalic acid is also a reducing agent, although weaker than ascorbic acid.)

Part 1: Effectiveness of Eight Solutions

The most effective treatment tested (**Table IV**) was a combination of a reducing agent (10% w/v sodium dithionite) and a chelating agent (1% w/v EDTA) with pH adjusted to 7.3. The next most effective treatments were a reducing agent alone (10% w/v sodium dithionite), an acidic chelating agent (20% w/v thioglycolic acid), and acid at low pH (2% w/v oxalic acid or 1% v/v phosphoric acid). The combination of 1% w/v EDTA and 0.5% w/v DTPA, two chelating agents, was not effective. The polymer PVP (1% w/v) was not effective alone and did not enhance the effectiveness of phosphoric acid.

Phosphoric Acid and PVP

Phosphoric acid did not remove any residue stain and only 23% of the chemical stain in 60 minutes (**Table IV**). Wight and Hanlan[9] tested 1% phosphoric acid on iron-stained textiles (wool and cotton) and found a change in reflectance comparable to that found here for chemically stained paper. The pH of 1% v/v phosphoric acid is estimated as 1.4. Such a low pH can damage cellulosic materials. (According to Burgess,[16] a pH of 4 or below can damage paper.)

It was proposed by Wight and Hanlan[9] that the polymer PVP could prevent iron ions from redepositing. PVP is known to inhibit dye from transferring between textiles.[17] Wight and Hanlan[9] found that PVP improved the removal of stains in some cases, such as the removal of iron stains from porcelain with sodium phosphate; in most cases, however, there was little or no improvement when PVP was added, and in particular they did not see a significant difference when they compared phosphoric acid with and without PVP, consistent with our results on paper. In our studies, 1% PVP alone did not remove stains from paper, and PVP did not enhance the ability of phosphoric acid to remove stains; in fact, the reflectance change for chemically-stained paper was less for 1% PVP and 1% phosphoric acid together than with 1% phosphoric acid alone.

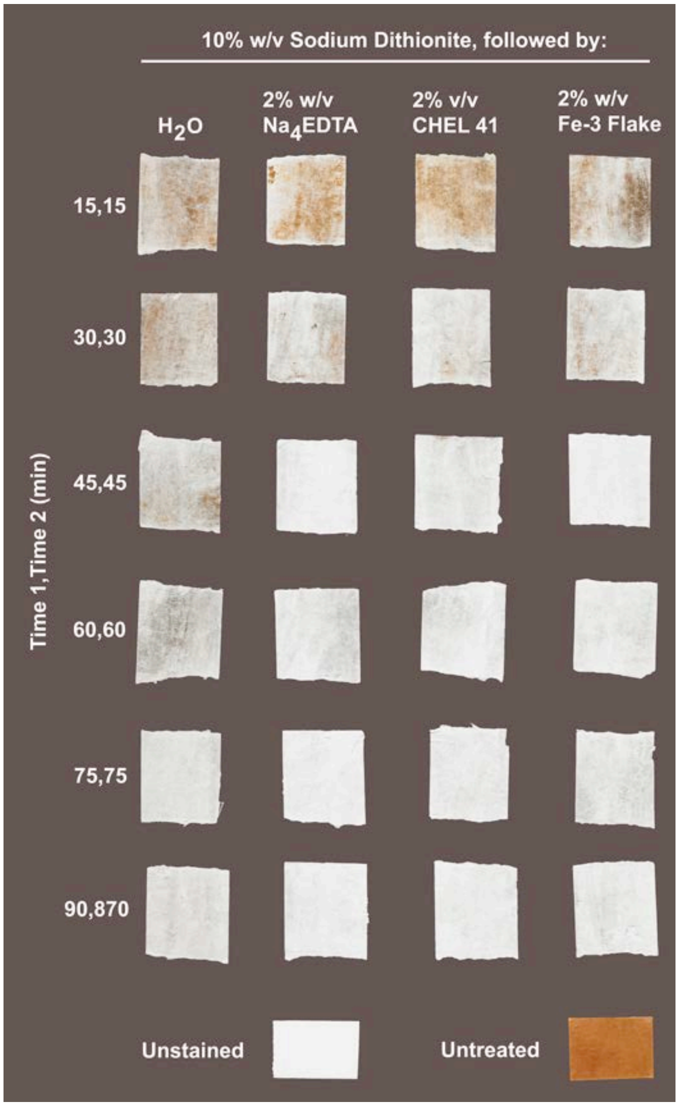

Figure 4. Samples treated with separate solutions of sodium dithionite and chelating agents. Times (left column) are in minutes. Treatment was done in two steps: first a 10% w/v solution of sodium dithionite, then either water or a solution of a chelating agent, either 2% w/v Na_4EDTA, 2% v/v CHEL 41, or 2% w/v Versene Fe-3 Flake. Samples were held at room temperature and kept from contacting the air. Control samples are shown at the bottom.

EDTA and DTPA

These are chelating agents. In general, a chelating agent dissolves a stain by adsorbing onto the surface of the stain particles, bonding to a metal ion in the stain particle, and then returning to the solution with the metal ion attached.[12] EDTA and DTPA at pH 9.2 were ineffective in dissolving rust stains. At high pH, iron oxyhydroxides have extremely low solubility, even with EDTA or DTPA present.[18]

Results with EDTA and DTPA at high pH in conservation have been mixed. Tilbrooke[19] looked at 5% Na_4EDTA at pH 13 for removing iron stains from sandstone. The solution at pH 13 had little effect even at high temperatures. Baker[20] tested 1% solutions of three salts of EDTA, Na_4EDTA (pH 9.6), Na_3HEDTA (pH 8.4) and Na_2H_2EDTA (pH 6.2), but none removed iron stains from paper. Wight and Hanlan[9] found that a mixture of 1% DTPA and 1% EDTA at pH 9.7-10 could remove some of the stain from unglazed porcelain tiles that had been artificially iron stained.

DTPA was tested for removing iron stains from wood from the shipwreck *Vasa*. Almkvist and Persson[21] treated samples for three years in 14 mM DTPA (pH 11), changing the solution at least every two months. The treatment removed over 90% of the iron. During treatment, the pH dropped to 9 before the solution was changed, because of the acid in the wood, so it is not clear what the pH was in the part of the wood being cleaned by the DTPA; it could have been considerably lower than 11. Another factor that may have contributed to the drop in pH is the adsorption of carbon dioxide.[22]

Oxalic Acid and Thioglycolic Acid

These act both as acids and as chelating agents to dissolve iron ions; oxalic acid is also a reducing agent which can help to mobilise the iron(III) into iron(II) with subsequent complexation and solution oxidation. These two properties, however, can work against each other – as the pH increases, unchelated iron ions become less soluble, but at the same time H^+ ions detach from the chelating agents, allowing soluble iron chelates to form.[12] As a result of the competition between acidity and chelation, the optimum pH for dissolving goethite in oxalic acid is 2.6[23] and for hematite is below 1.5.[24]

Both oxalic acid and thioglycolic acid removed significant amounts of the chemical stains, but were less successful with the residue stain. This suggests that they readily dissolved some components of the residue stain, but could not dissolve other components, at least during the time of the experiment. The drawback of these treatments for cellulose is the same as for phosphoric acid – the low pH. But since thioglycolic acid and oxalic acid also function as chelating agents, they might also be effective at higher pH, in a range safer for cellulose. There are a few examples of iron stains removed in conservation by oxalic acid on wood,[25] cotton[26,27] and paper.[28] Thorn[29] found thioglycolic acid to be effective at pH 8 for removing iron stains from marble, and Howie[30] used it at pH 3 to remove iron compounds in the treatment of fossils.

Dithionite, and Dithionite plus EDTA

These were the most successful treatments from the survey of eight test solutions: 10% w/v sodium dithionite with or without 1% w/v EDTA. Both dithionite alone and dithionite plus EDTA dissolved almost as much chemical stain as thioglycolic acid. Dithionite plus EDTA was the most successful treatment for dissolving residue stain. Because of the clear superiority of dithionite plus EDTA at dissolving the residue stain, it was decided to pursue the study of dithionite plus a chelating agent for the second part of the study.

Part 2: Effectiveness of Dithionite and Chelating Agents

The dithionite ion is a strong reducing agent with a standard reduction potential of -1.12 V for the following reaction:

$$2SO_3^{2-} + 2H_2O + 2e^- \rightleftharpoons S_2O_4^{2-} + 4OH^-$$

where SO_3^{2-} is the sulfite ion and $S_2O_4^{2-}$ is the dithionite ion.[31] It is a strong enough reducing agent to reduce Fe(III) in iron oxyhydroxides and form more soluble Fe(II)-containing compounds. The overall reaction of the dithionite ion with iron oxyhydroxides at neutral or slightly acidic pH is:

$$2FeOOH + S_2O_4^{2-} + 4H^+ \rightarrow 2Fe^{2+} + 2HSO_3^- + 2H_2O$$

where HSO_3^- is the hydrogen sulfite ion. Dithionite is used to extract iron oxides from soils by reducing Fe(III) to Fe(II).[12] In the combination of EDTA and dithionite, Rueda et al.[32] argue that both EDTA and dithionite adsorb on the surface and work together to dissolve iron ions. The use of dithionite in artifact conservation, both alone and with EDTA, has been reviewed by Selwyn and Tse.[31]

The degradation of dithionite has also been discussed by Selwyn and Tse.[31] In the presence of dissolved oxygen, the dithionite ion readily reacts with it as given by:

$$2S_2O_4^{2-} + O_2 + 2H_2O \rightarrow 4SO_3^{2-} + 4H^+.$$

The dithionite ion is oxidized to the sulfite ion, oxygen is reduced, and the solution becomes more acidic. The dithionite ion readily reacts with water, even in the absence of oxygen, and decomposes to various sulfur-containing species such as hydrogen sulfite, thiosulfate ($S_2O_3^{2-}$), hydrogen sulfide (H_2S), polysulfides (H_2S_x), and elemental sulfur (S). These new species react with dithionite ions and further deplete them. Sodium dithionite decomposes at room temperature, although more slowly at higher pH than at lower pH, and more slowly at room temperature than at higher temperatures.[33] As more and more dithionite ions are either oxidized by air or decompose, there are fewer dithionite ions remaining to act as reducing agents in the reduction of iron(III) compounds to more soluble iron(II) compounds. Moreover, sulfur-containing decomposition products can cause problems later if they are not fully rinsed out, because at high humidity they can oxidize and release sulfuric acid that will attack cellulose.[21]

The results of the experiments to investigate the effects of temperature and air showed the importance of proper handling of dithionite solutions. Dithionite should be used at room temperature with minimum exposure to air because the solutions degrade when heated and when exposed to air (**Figure 1**).

The initial tests of the effectiveness of sodium dithionite and chelating agents showed that samples treated with dithionite plus chelating agent turned yellow by the next day if they were not rinsed in distilled water after the treatment. Thorough rinsing is needed to remove soluble Fe(II) from the samples. Without washing, the Fe(II) can be reoxidized to Fe(III), leading to discolouration or colour reversion.[31] Although a single rinse was sufficient for these samples, a complex archaeological wood-iron object under treatment might require several rinses to ensure the removal of soluble iron ions. Rinsing should be done until the rinse water remains clear or tests negative for Fe(II) using test strips.[34] It should be remembered that the rinsing is controlled by diffusion processes and so a doubling of the removal factor will take four times the washing time.

The concentration of chelating agent is not critical, at least over the ranges tested here, 2% to 4% (**Figure 2**). Reducing the pH of the solutions from about 6 to 5 with acetic acid dissolved the stains faster, but even at the higher pH most of the stain was removed in 45 minutes (**Figure 2** and **Figure 3**). There was no significant difference between the different chelating agents tested (EDTA, DTPA, DHEG) (**Figure 2** and **Figure 3**). Using dithionite plus EDTA together in the same solution was not significantly different than using a two-step treatment with dithionite first and EDTA second (**Figure 4** compared to **Figure 2** and **Figure 3**). (This last conclusion is at odds with the results of Baker,[20] who found that the two-step treatment was better than a combined treatment in removing iron stains from chemically stained filter paper.) In the two-step treatment tested here, the dithionite appeared to remove the bulk of the staining while the chelating agent appeared to clean up some staining that the dithionite did not remove.

Chelating agents and reducing agents act together in dissolving iron ions from iron oxides.[12,15,32] These conclusions are based on studies comparing a reducing agent or a chelating agent alone with a combination of the two. Aside from Baker's work,[20] other publications were not found that compare whether chelating agents and reducing agents together are more effective than a two-step treatment using the two separately. It is possible that a two-step treatment is better because, for example, one species might interfere with the other in some way, such as by blocking the surface. One advantage of the two-step approach is that the dithionite solution can be replaced frequently without wasting the chelating agent.

One issue that was not addressed in this study is bleaching. Sodium dithionite can reduce yellow oxidation products and so may bleach organic materials.[31] Conservators should be aware of this and if it is of concern with an object, then tests should be done first.

The effect of dithionite on newsprint that contained cellulose and lignin was tested by Hawley et al.[8] Little or no change to the newsprint samples was observed, and this suggests that wood and composite objects would not be significantly affected by dithionite. Treatment based on 10% w/v sodium dithionite and 1% w/v Na_4EDTA has been used to reduce iron staining on archaeological wood at Parks Canada, with no evidence of bleaching.

Conclusions

This research supports the use of a solution of sodium dithionite together with a chelating agent for removing rust stains on wood-iron composite objects. These solutions effectively removed iron stains from paper stained by soaking in an iron solution and from paper coated with iron corrosion products taken from artifacts. The stain removal was usually completed after a couple of hours, but was slow enough that the change in colour could easily be monitored visually. The reactions take place at room temperature and at a pH near neutral and so will not likely damage the wood or the iron in artifacts. The main constraint in using this process is that air should be excluded from the dithionite solution, which could be difficult when large artifacts are being treated. If air is not excluded, the solution would need to be replaced more frequently, adding to the cost of treatment. (In 2014, the price of sodium dithionite was about $300 per kilogram and that of tetrasodium EDTA was about $200 per kilogram.) It should be noted that this work was based on use of a 10% w/v solution of dithionite, as used by previous workers, and it was not intended here to determine its optimal concentration.

Based on this research, the following process is suggested for removal of iron stains from waterlogged wood and wood-iron composite objects at room temperature. This process is to be used after the objects have been mechanically cleaned and before they are placed in a polyethylene glycol solution in preparation for freeze-drying. In this method, a fresh solution of 10% w/v sodium dithionite and 1% w/v Na_4EDTA is prepared with a sufficient volume to cover the object. The object is placed in the solution in a covered container and monitored visually as the orange coloured stain disappears. This may occur in as little as 30 minutes or may take several hours. Then the object is thoroughly rinsed in successive baths of deionized water until the rinse water is clear; this may take several days.

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