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Photograph: Detail from 'Bridge No. 2' from the series *Rust Never Sleeps*, John Moore, 1996

CHLORIDE CALAMITIES: ASSESSMENT OF RESIDUAL CHLORIDE ANALYSIS TO COMPARE IRON DESALINATION METHODS

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Abstract

An analytical protocol was designed for the analysis of chloride ions in treatment solutions as well as in solids after desalination to avoid chloride loss during the digestion process. The alkaline sulphite method originally suggested by North and Pearson (North and Pearson 1975) was tested with varying concentrations of sodium hydroxide and sulphite under nitrogen. The excellent desalination efficiency of sodium hydroxide solutions under de-aerated conditions reported by Al Zahrani (1999) could not be confirmed, but this technique seems to be more efficient than alkaline sulphite. Results suggest the use of oxygen-free sodium hydroxide as a desalination technique should be more suitable for mass treatment of terrestrial iron.

Keywords: Iron desalination, nitrogen, sodium hydroxide solutions, alkaline sulphite method, chloride analysis

Introduction

The corrosion of archaeological iron objects after excavation is a well known problem in the archaeology and conservation community since the 19th century (Krause 1882; Scott and Eggert 2009). This is particularly true when iron is excavated and left to dry and akaganéite has formed as the main corrosion product (Reguer et al. 2007). It is well known that the chloride containing phase akaganéite is responsible for post excavation damage phenomena (Zucchi et al. 1977).

North and Pearson developed the alkaline sulphite method in 1975 (North and Pearson 1975) and it has proven to be effective in desalinating and stabilizing iron objects (Rinuy 1979, Rinuy and Schweizer 1982, Watkinson 1983 and 1996, Al Zahrani 1999). Desalination is achieved in an alkaline medium by exchanging OH⁻ with Cl⁻ in the akaganéite (Ellis et al. 1976) via a dissolution and precipitation process (Cornell and Giovanoli 1990). In the case of desalination of terrestrial iron, the sulphite acts as an oxygen scavenger (Gilberg and Seeley 1982, Gilberg 1987). Considering the passivating properties of sodium hydroxide for iron in an aqueous solution, what is the exact role of the sulphite in the desalination process of archaeological iron objects? Does the presence of sulphite make a difference or is sodium hydroxide alone sufficient? De-aerated conditions using nitrogen for desalination with sodium hydroxide have been previously investigated (Al Zahrani 1999, Watkinson and Al Zahrani 2008). Attempts to simplify the alkaline sulphite desalination process have been made using room temperature instead of elevated temperature, or by

using less concentrated sulphite and sodium hydroxide solutions (Stawinoga 1996, Schmidt-Ott and Oswald 2006). The current project compares the extraction efficiency of solutions of less concentrated sodium hydroxide, with or without the presence of sulphite, at room temperature under nitrogen. Since the complex system of corrosion products on the surface of an archaeological iron object cannot be readily reproduced, the experiments are conducted on real archaeological iron objects.

To assess desalination efficiency, chloride content in the desalination solutions and residual chloride content in the iron objects was determined. Particular attention was given to the analytical protocol used to determine the residual chloride concentrations in the solids. Therefore, this paper has two focal points: the analysis of the chloride content in treatment solutions and desalinated objects using photometry, and the replication and variation of the de-aeration of sodium hydroxide experiments as reported by Al Zahrani (1999).

Chloride Determination – Problems and Solutions

Background

To date, the focus in conservation literature has been on analytical methods suitable for chloride analysis in desalination solutions and desalinated objects. In contrast, sample preparation has been less important. Ellis et al. (1976) report total chloride loss in the form

Reference	Preparation	c	T °C	Time	Cl ⁻ Analysis
Al Zahrani 1999: 182	HNO ₃	27%	18 °C	3 d	ion-selective Electrode
Drews et al. 2004: 250	HNO ₃	25%	hot plate	2 d	Pot. Titration/ IC
Rinuy 1979: 139	H ₂ SO ₄ / HNO ₃	2.7%/ n. r.	n. r.	n. r.	Pot. Titration
Rinuy and Schweizer 1982: 163	Mechanical + AS	Each 0.5 mol/l	50°C	n. r.	Pot. Titration (?)
Watkinson 1983: 88	H ₂ SO ₄	20%	n. r.	n. r.	n. r.
Watkinson 1996: 209	HNO ₃	n. r.	n. r.	n. r.	ion-selective Electrode
Wang et al. 2008	Water	-	n.r.	3 d	IC
Watkinson and Al Zahrani 2008: 80	HNO ₃	5 mol/l	n. r.	n. r.	ion-selective Electrode

Table 1. Overview of published methods in the conservation literature for determination of chloride content in iron objects. (c = concentration; d = days; Pot. = Potentiometric; IC = Ion Chromatography; n. r. = not reported; AS = alkaline sulphite solution).

of volatile hydrogen chloride, caused by excessive acid when desolving akaganéite powder in sulphuric acid (H₂SO₄, 20% w/w) and, therefore decided to use sealed ampoules for digestion. In addition, Volkwein and Dorner mention an old-fashioned digestion protocol for chloride-contaminated concrete that involved boiling the samples in a solution of 38% nitric acid for 30 minutes. After boiling, 20% of the initial chloride concentration had vanished (Volkwein and Dorner 1986). In contrast, digestion for 10 minutes in cold nitric acid (27%) followed by three minutes in hot, but not boiling nitric acid of the same concentration, is short enough to not interfere with the chloride concentration (Deutscher Ausschuss für Stahlbeton [DAfStb] 1989). In general, iron nails need longer digestion time, which may allow chloride to evaporate as hydrochloric acid. Since this problem has not been adequately addressed in conservation science, our aim is to clarify this situation. The results of these findings may be of great importance for the conservation community.

Analytical Procedure

Determination Method for Chloride Ions

In the current research project, photometric analysis is used for chloride determination as suggested by Wunderlich (Wunderlich 2000) due to its capability to determine small amounts of chloride with deviations of less than 2.5% (Gottwald and Heinrich 1998). The device used for this procedure is a Spectronic Genesys 10 UV-Vis Split-beam Spectrophotometer (with an accuracy of 0.5% deviation). The chemical reaction for chloride determination used in this project is the quantitative reaction of Hg(SCN)₂ with chloride to a chloromercurate(II) complex ion, and the freed thiocyanate ions (SCN⁻) react with Fe³⁺ to the red iron thiocyanate complex (for details see Florence and Farrar 1971).

Validation of own Digestion and Determination Method

For validation of the measurements used in this study, iron powder was digested in sulphuric acid (20%) with added sodium chloride solution of known concentration. After the iron powder was dissolved, interfering Fe²⁺ ions were oxidized to Fe³⁺ ions (2Fe²⁺ → 2Fe³⁺ + 2e⁻) by hydrogen peroxide (30%), according

to the equation H₂O₂ + 2 e⁻ + 2 H⁺ → 2 H₂O. Excessive H₂O₂ was expelled by boiling for 30 minutes. After cooling, the volume of the sample solution is measured. Subsequently, the sample is prepared for photometric analysis as per Florence and Farrar (1971), and directly measured. Three measurements give a mean of 1.10 mg/l chloride (standard deviation of ± 0,042) in contrast to the reference value of 1.0 mg/l chloride. The difference of about 0.1 mg/l can be expressed as an error of 10%, which is acceptable considering the numerous interfering ions in the analytes.

Problems of Other Digestion Strategies

After checking the validity and reliability of our own measurements, the protocols used by other researchers were examined. Table 1 shows some published digestion protocols for determination of residual chloride in excavated terrestrial iron objects (with the exception of Drews et al. 2004, which discusses marine objects).

As shown in Table 1, nitric acid is typically used for this kind of application. In general, chloride ions may partially react with nitric acid to form gaseous nitrosyl chloride. If nitrosyl chloride evaporates, an underestimation of chloride concentration can occur. Therefore, nitric acid is a poor choice to dissolve chloride-contaminated iron, if the potential chloride loss is not avoided by other means. In addition, there is the difficulty of excessive iron ions and excessive mineral acid. Therefore, as is the case with many analytical methods, a pre-treatment of the sample is required. For example, Al Zahrani precipitates iron with sodium hydroxide before analysis. This method may induce a loss of chloride ions because the surface of freshly precipitated iron hydroxide is known to be a powerful absorber of chloride ions (Lahann 1976). Potentiometric titration is also disturbed by excessive iron ions (Rinuy 1979). Water is not considered as an adequate solubilising agent for chloride in corrosion layers or objects as suggested by Wang et al (Wang et al. 2008), since structural chloride ions cannot be removed from akaganéite with water (Ellis et al 1976). Furthermore, ion chromatography usually requires the eluent to be neutralized. In addition excessive iron ions may require a specific sample preparation prior to analysis. It should be noted that photometric determination of chloride ions by the previously mentioned protocol interferes with nitrosyl thiocyanate, which is red in colour like the Fe(SCN)₃

complex (Jander and Blasius 1985).

Replication of Other Digestion Strategies

Using our validated analytical method and an iron powder sodium chloride mixture, the digestion protocols of Al Zahrani (1999) and Drews et al (2004) were reproduced to check for potential chloride loss. Both procedures were reproduced using sulphuric instead of nitric acid. After three days at room temperature, the iron powder was solubilized inside the beakers covered with watch glass as per Al Zahrani (1999). After oxidation and heating for 30 minutes, no loss of chloride could be detected. In contrast, heating for two days at 80°C as suggested by Drews et al (2004) causes loss of chloride from the iron powder–sodium chloride mixture. Covering of the beaker influences results: no cover plate allows loss, a watch glass prevents it, but the accuracy of the measurement is probably affected by leakage. Pressure-resistant bottles with special gas tight closure heads (DURAN, Germany) prevent chloride loss, even after 48 hours (see Table 2). Obviously, the standard deviation can be better evaluated if it is considered in relation to the mean by the so-called variation coefficient⁽¹⁾. As can be seen in Table 2, the bottles with a gas tight closure exhibits the highest reliability (i.e. smallest variation coefficient) and highest validity (least difference between mean and reference value).

Conclusion Concerning Digestion Strategies

The above review and laboratory work show that all data reporting residual chloride remaining in desalinated iron objects using digestion strategies based on length of time and hot dissolution without a cover for the solutions used, clearly should be subject to caution. In addition, interpretation of the results without a detailed report about the digestion (see Table 1) is questionable.

EXPERIMENTAL

In the following section of the paper, the replication and variation of the desalination experiments with de-aerated sodium hydroxide solutions based on Al Zahrani (Al Zahrani 1999) are reported, as well as the analysis of desalination solutions and residual chloride analysis of iron nails.

Desalination Experiments

In contrast with Al Zahrani, sodium hydroxide, pure sodium sulphite and alkaline sulphite solutions were

tested in a nitrogen atmosphere to examine the role of sodium sulphite on desalination success (if not needed as an oxygen scavenger). Furthermore, the desalination was not terminated until all extractable chloride ions had washed out. This required four treatment baths of 60 days for each test.

Samples

The iron nails used were excavated in 1979 from the Roman site 'Köngen' near Esslingen, Germany. Seven sets of 100 g (± 3 g) iron nails of different sizes (on average around 10 nails) with remaining iron-cores were used. The majority of the nails were stored at -20°C and had completely dried out. For the purposes of this study, they were superficially cleaned of loose soil particles with air-abrasion.

Desalination solutions and procedure

The solutions used and their concentrations are as follows: alkaline sulphite, 0.5 mol/l sodium hydroxide (NaOH) and 0.5 mol/l sodium sulphite (Na₂SO₃) (North and Pearson 1975); diluted alkaline sulphite, 0.1 mol/l NaOH and 0.05 mol/l Na₂SO₃ (Schmidt-Ott and Oswald 2006); and NaOH, 0.1 and 0.5 mol/l. One litre of solution was used for each 100g set of nails to ensure comparability of results. Two tests were undertaken, each with a 100g set of nails, except for the 0.1 mol/l sodium hydroxide solution, where only one 100g set of nails was used. After 60 days, the chloride content of the solutions was determined. At a concentration of 0 to 2 mg/l chloride the desalination was considered to be complete. After treatment, the objects were soaked in warm deionised water until the pH was neutral, followed by drying.

Inert atmosphere

The containers with the nails and the desalination solutions were placed in a Binder VD 115 vacuum drying oven (Germany) purged with N₂ in 99.999 %-mol quality (Air Liquide, Germany). Before running the experiments, the oven was evacuated twice and flushed with nitrogen gas. The experiments were conducted at room temperature (20 °C \pm 1 °C).

Pre-treatment of desalination solutions for determination of chloride-content

Since sulphite interferes as reducing agent with the protocol as described, it has to be oxidized, and the sample solution has to be acidic. Therefore, a solution

Covering	Reference Amount in ppm Cl ⁻	Measured Amount in ppm Cl ⁻	Mean in ppm Cl ⁻	Standard Deviation in ppm Cl ⁻	Variation coefficient in %
none	1.0	0.413	0.31	0.17	53.96
	1.0	0.117			
	1.0	0.400			
not gastight (watch glass)	1.0	1.344	1.24	0.20	17.74
	1.0	1.106			
	1.0	0.945			
gastight (special bottle)	1.0	1.153	1.06	0.11	10.08
	1.0	1.082			
	1.0	0.943			

Table 2. Demonstration of chloride loss by hot digestion over 48 hours with a solution temperature of 85°C.

containing 5 mol/l nitric acid and 10% hydrogen peroxide has to be added in the ratio 1:1 to the sample solution (Weker and Trojanowicz 1987, Beaudoin and Bertholon 1994). For complete oxidation, the sample stands at room temperature for 24 hours in a closed bottle. The error associated with this pre-treatment can be up to 10%, which, as previously discussed, is acceptable. The pH of desalination solutions containing only NaOH is adjusted by the reagents and needs no further preparation.

Determination of chloride ion concentration

The determination of the chloride ion concentration of the desalination solutions and in the desalinated objects was carried out with photometric analysis and the protocol described above.

Determination of chloride-content of desalinated iron objects

Prior to analysis to determine chloride content, 71 desalinated nails were entirely cut into small cubes approximately 4 mm-long, with a weight of approximately 0.1g each. This was deemed to be a better way to deal with the variation in chloride distribution in the nails. Acceleration of the solubilization process was facilitated by digesting small pieces of the nails, and, given the quantity of material to be analyzed, this method also used less sulphuric acid. 66 of the 71 nails

were large enough for two groups of samples to be cut from each nail. The two groups consisted of randomly selected pieces from each nail. The chloride content from these two groups was analyzed. The remaining 5 nails were too small to allow two groups of samples, therefore these 5 nails were each digested whole to determine their residual chloride content. The mean chloride content was determined in ‰. In contrast to iron powder as specimen, the sample solution had to be centrifuged after oxidation for five minutes to separate it from insoluble matter.

RESULTS OF DESALINATION EXPERIMENTS UNDER A NITROGEN ATMOSPHERE

Chloride-content of desalination solutions

The results in Table 3 indicate that the diluted alkaline sulphite solution (DAS) extracted more chloride than the alkaline sulphite (AS) solution, and that there appears to be no significant difference in extraction between 0.5 and 0.1 molar solutions of sodium hydroxide. Data from this part of the experiment show that pure sodium hydroxide solutions without the addition of sulphite extract slightly more chloride in a nitrogen atmosphere, but the difference in concentration of the sodium hydroxide concentration does not seem to play a significant role.

Solution	Bath 1	Bath 2	Bath 3	Bath 4	Total	Mean	Standard Deviation
AS 1	22.22	2.96	1.48	0.00	26.66	25.92	1.05
AS 2	22.22	1.48	1.48	0.00	25.18		
DAS 1	27.41	2.22	4.44	0.00	34.07	37.03	4.19
DAS 2	34.81	2.96	2.22	0.00	39.99		
OH ⁻ 0.5 1	23.07	3.44	1.59	1.59	29.69	41.18	16.24
OH ⁻ 0.5 2	41.96	6.41	2.70	1.59	52.66		
OH ⁻ 0.1	30.85	4.56	1.96	1.96	39.33		

Table 3. Chloride extracted in ppm by alkaline sulphite and sodium hydroxide solutions, each in two test series (one treatment bath = 60 days). AS = Alkaline Sulphite solution according to North/ Pearson (1975), DAS = Diluted Alkaline Sulphite according to Schmidt-Ott/ Oswald (2006), OH⁻ 0.5 = Sodium hydroxide 0.5 mol/l, OH⁻ 0.1 = Sodium hydroxide 0.1 mol/l

Column	1	2	3	4	5
Treatment	Absolute weight of objects	Absolute Cl ⁻ extracted by treatment	Absolute residual weight of Cl ⁻ in objects	Absolute weight of chloride in objects	Relative amount of Cl ⁻ extracted by treatment of total Cl ⁻ in objects
	in kg	in mg	in mg	in mg	in %
AS	0.10058	26.66	19.48	46.14	58
AS	0.10104	25.18	18.60	43.78	58
MEAN	0.10081	25.92	19.04	44.96	58
DAS	0.10005	34.07	15.40	49.47	69
DAS	0.10124	39.99	32.12	72.11	55
MEAN	0.10065	37.03	23.76	60.79	62
OH ⁻ 0.5	0.10053	29.69	14.80	44.49	67
OH ⁻ 0.5	0.10190	52.66	22.00	74.66	71
MEAN	0.10122	41.18	18.40	59.57	69
OH ⁻ 0.1	0.10310	39.33	30.34	60.03	49

Table 4. Extracted chloride in absolute and relative amounts to assess desalination success. AS = Alkaline Sulphite solution according to North/ Pearson (1975), DAS = Diluted Alkaline Sulphite according to Schmidt-Ott/ Oswald (2006), OH⁻ 0.5 = Sodium hydroxide 0.5 mol/l, OH⁻ 0.1 = Sodium hydroxide 0.1 mol/l

Chloride-content of desalinated iron objects

To evaluate the desalination, in Table 4, the reported weight of extracted chloride by treatment (column 2) and the residual chloride (column 3) are added to get the total amount of chloride in the object (column 4). Extraction efficiency is calculated in terms of relating the chloride amount extracted by treatment to the total amount of chloride in the object expressed in % (column 5). The chloride content of each 100g batch is calculated by relating the individual chloride contents to the masses of the corresponding objects. For example, the residual chloride content of an object weighing 5g will not influence the mean residual chloride content as much as the content of an object weighing 30g.

Table 4 provides the extraction pattern as a function of total chloride in the iron. A sodium hydroxide solution of 0.5 mol/l extracts the most chloride by treatment (column 2), and exhibits the least amount of residual chloride (column 3). In contrast, sodium hydroxide 0.1 mol/l shows an extraction amount similar to the other solutions during desalination (column 2), but the weight of remaining chloride is the highest for all objects tested (column 4). Further, the alkaline sulphite solutions show similar extraction behaviour, but the level of extracted chloride is slightly less compared to the other desalination solutions.

With regard to the quality of the data, the average variation coefficient of the 66 means resulting from two residual chloride measurements per nail described above (with an average standard deviation of 0.054 %) is 21.63%^[1]. This means that the measurements show a very good reliability and reproducible results, though archaeological finds were used as specimens and a special sample preparation strategy was used. In general, the chloride contamination of the iron finds from the Roman site 'Köngen' seems to be relatively low. Nevertheless, this comparatively low chloride level is still causing post excavation active corrosion.

Discussion

Since post excavation corrosion appears to be caused by the residual chloride, the amount of residual chloride after desalination should be the main criterion for evaluating the treatment. The least amount of residual chloride in the Köngen objects was found in those desalinated under nitrogen with 0.5 mol/l sodium hydroxide, alkaline sulphite, and diluted alkaline sulphite, while the most chloride was found in objects desalinated with 0.1 mol/l sodium hydroxide. However, the efficiency of the methods does not vary that much. For alkaline sulphite, our data for Köngen (58% extraction of total chloride) are lower than the ca. 70% of Rinuy and Schweizer (Rinuy and Schweizer 1982), the ca. 87% of Watkinson (Watkinson 1996) and the 96% of Al Zahrani (Al Zahrani 1999). The desalination efficiency of 0.5 mol/l sodium hydroxide (69% extraction of total chloride) under nitrogen is confirmed, but not the 99.5% extraction efficiency cited by Al Zahrani. Considering the absolute residual chloride of 0.5 mol/l sodium hydroxide (18.4 mg), alkaline sulphite (19 mg) and diluted alkaline sulphite (23.8 mg), sulphite concentration does not seem to affect the desalination as expected (see Watkinson and Al Zahrani 2008).

Evaluating the data reported here, it should be kept in mind that significant differences between desalination strategies are always difficult to compare due to the inherent heterogeneity of archaeological iron samples. Firstly, the chloride distribution inside objects from the same site can vary significantly. Secondly, the structure of the corrosion products in each object plays a major role in the diffusion processes. An accurate analysis of desalination solutions is difficult to achieve due to interference with sulphite, iron, mineral acid and other ions.

Conclusion

The data reported here show that the digestion strategy can affect the results of residual chloride analysis, and should be measured carefully to avoid loss into the air during hot acid digestion. If not accurately measured, the result is biased in terms of overestimation of the desalination by treatment method. In the aqueous desalination treatments described by the authors, chloride-free objects were impossible to achieve.

Since the sulphite component does not need to perform its deoxygenation function under a nitrogen atmosphere, and it neither interfered nor facilitated the desalination, an option is to desalinate with high concentrated sodium hydroxide solutions. However, the desalination solutions with a reduced NaOH concentration also show similar results, and should be noted as further alternatives. Several advantages are to be mentioned: using nitrogen helps to save costs by reducing or omitting chemical agents and saving time in weighing and disposing — these benefits meet the requirements for mass treatment of archaeological iron objects.

This work will be continued since sizeable amounts of data allow a thorough evaluation of desalination treatments. In the near future, more experiments will be conducted regarding the concentration of sodium hydroxide, as well as the role of sulphite in desalination experiments under aerated and de-aerated environments, for example, those under vacuum.

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Endnotes

[1] The variation coefficient is a relative measure which expresses the standard deviation as a percentage of the mean. It is calculated as per (standard deviation*100/ mean) in %. The smaller the variation coefficient, the better the data.

Materials

All chemicals used were of high purity, analytical grade (pro analysi), the water used was deionised. All chemicals were purchased at:

Carl Roth GmbH + Co. KG
Schoemperlenstraße 1-5, 76231 Karlsruhe, Germany
Telephone: 0049-721-56060
<http://www.carl-roth.de>

Mercury thiocyanate
VWR International GmbH
(Hilpertstraße 20a, 64295 Darmstadt
Telephone: 0049-6151-39720
http://www.chemie.de/firmen/e/12501/vwr_international_gmbh.html

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Gerhard Eggert received a PhD in chemistry from the University of Bonn with experimental work in electrochemistry. From 1985-1998 he was Head of the Conservation Department of Rheinisches Landesmuseum Bonn. He is currently a Professor for Objects Conservation at the State Academy of Art and Design Stuttgart, with research interests in the manufacture, decay, and conservation of glass and metal artifacts.