DEPARTMENT OF CONSERVATION

DESALINATION OF ARCHAEOLOGICAL IRON OBJECTS IN VACUUM

Aleksi Pienimäki

Degree project for Master of Science with a major in Conservation
2023, 60 HEC
Second Cycle
2023:22

Desalination of Archaeological Iron Objects in Vacuum

Aleksi Pienimäki

Supervisors:

Bo Anders Lagerqvist
Carl Brädde

Degree project for Master of Science with a major in Conservation

UNIVERSITY OF GOTHENBURG
Department of Conservation

ISSN 1101-3303
2023:22

UNIVERSITY OF GOTHENBURG
Department of Conservation
P.O. Box 130
SE-405 30 Gothenburg, Sweden

http://www.conservation.gu.se
Fax +46 31 7864703
Tel +46 31 7864700

Master's Program in Conservation, 120 ects

Author: Aleksi Pienimäki
Supervisor: Bo Anders Lagerqvist & Carl Brädde

Title: Desalination of Archaeological Iron Objects in Vacuum

ABSTRACT

This work investigates the efficiency of commercially available vacuum containers as a physical deoxygenation method for desalination solutions for archaeological iron. Other factors are investigated as well, such as the effect of cleaning the objects of their corrosion crusts before treatment and drying them between subsequent treatment baths. While only pre-cleaning could be shown to have a statistically significant effect on residual chloride concentrations, use of vacuum shows promising results and deserves to be investigated further.

Title (original language):
Language of text: English
Number of pages:
3-5 Keywords: Archaeological iron, desalination, vacuum

ISSN 1101-3303
2023:22

Contents

Acknowledgments

I would like to thank my supervisors, Bo Anders Lagerqvist and Carl Brädde for their patience and many good suggestions during the long writing process. I would also like to thank my first supervisor, Stavroula Golfomitsou, for helping me get this project started several years ago.

I am grateful towards my employer at the time of practical part of this thesis, Kiruna Centre for Conservation of Cultural Property, for enabling this work. Without their resources it would have been impossible to conduct the experiments.

This work has been financially supported by Märta, Gunnar and Arvid Bothén’s Trust.

1. Summary

This study investigates the feasibility of commercially available vacuum containers as a way of deoxygenating desalination solutions for archaeological iron. 128 discarded archaeological iron nails were divided into 16 batches of 8 nails. The groups had an average weight close to 160 grams.

Three treatment factors, two of which were binary and one with three levels, were randomly assigned to the batches:

1. Solution: sodium hydroxide (0.5 M NaOH), alkaline sulphite (0.5 M NaOH + 0.05 M Na_2SO_3) and reverse-osmosis water.
2. Pressure: partial vacuum or ambient.
3. Cleaning stage: pre-cleaned or uncleaned

Partial vacuum was achieved using commercially available vacuum containers. Cleaning was carried out using air-abrasives. The material was condition assessed before and after treatment to document deterioration due to treatment.

Desalination was followed by plotting the chloride concentration of each batch against square root of time. When the resulting plot deviated from linearity, solution was changed. When chloride concentration remained ≤ 5 mg/L over a period of four weeks, the extraction was considered negligible, and the treatment terminated. Dissolved oxygen, pH and conductivity was measured weekly along with the chloride concentration.

After termination the batches were allowed to dry, and desalination was re-initiated to see if drying would result in further release of chlorides. Once no more chlorides could be extracted, the specimens were subjected to destructive residual chloride analysis. Treatment efficiency was evaluated based on residual chloride concentrations. Objects treated with reverse-osmosis water did not have time to finish, so their residual chloride concentrations could not be analysed.

Lowest residual chloride levels were achieved using sodium hydroxide on pre-cleaned samples in vacuum on. A three-way ANOVA test was conducted with the residual chloride data to check for statistical significance of the results. The only factor that reached statistical significance at an α level of 0.05 was pre-cleaning. More testing is necessary to verify the effect of other factors.

The significance of these findings is discussed from a theoretical perspective. There is a gap between desalination research and practice that new information alone cannot mend. Possible reasons and remedies for the current situation are brought up.

2. Introduction

2.1.General background

One can wonder what motivates yet another technical study on the desalination of archaeological iron, considering how many commendable yet inconclusive investigations have already been carried out. Many current desalination methods can be traced back to the late 1800s. Such a long tradition begs the question if there is anything genuinely new to be discovered in the field.

However, despite all this research, we still need an ideal solution to the post-excavation chloride-driven corrosion problem. All current methods have side effects, and none guarantees stability – perhaps except for subcritical treatment, though this remains to be seen. At the same time, objects susceptible to post-excavation corrosion keep getting exhumed, and previously treated material is regularly sent for retreatment due to recurrent corrosion. Postponing treatment in the hopes of a possible future breakthrough is not a viable option (Appelbaum 2007: 371-72). Rust never sleeps.

Desalination is an unrewarding step in the conservation treatment of archaeological iron. It is a lengthy procedure that does not cause any apparent improvement in the condition of the treated material. On the contrary: some material suffers flaking and even disintegration due to delaminating corrosion layers (Keene 1991: 260-61; Koh and Skogstad 2015; Rimmer 2010: 157-66; Selwyn and Logan 1993: 805; Selwyn and Argyropoulos 2005) and one cannot but wonder what dissolved substances cause the rich brown colour distinctive for the first couple of treatment baths for previously untreated material. What else is being extracted besides chloride?

The evolution of the treatment is followed by measuring the concentration of the invisible chloride ion in the solution. It is often carried out with limited chemical competence using a methodology not intended for solutions with high ionic strengths, complex, unknown sample matrixes, and high pH. From such demanding solutions, the endpoint of the treatment could be indicated by a chloride concentration of ≤ 5 mg/L (Loeper-Attia and Weker 1995; Rimmer et al. 2013) - a very low number to be measured reliably, quickly, and perhaps most importantly, affordably.

Chemicals routinely used in the process are corrosive and burn the eyes and the skin. Chloride analysis often necessitates further chemicals (Greiff and Bach 2000; MacLeod 1984; North 1987; Scott and Eggert 2009: 141; Selwyn 2001; Wang et al. 2008), and more are used when the solution is neutralised for disposal. On conservation standards, the treatment is carried out on a large scale, so the chemical load brought about by the desalination treatment of iron can become significant. This can seem difficult to motivate in the face of increasingly stringent environmental, health, and safety standards.

Finally, after all the trouble, successful treatment does not manifest itself in any way, and not even our best efforts are guaranteed to stabilise the most susceptible objects (Watkinson 2010; Watkinson et al. 2013: 414). We usually never know how much the treatment has contributed to the stability of the material. In the case of recurrent corrosion, we do not get to see how much worse the situation would be without treatment.

Desalination can seem to be little more than guesswork in the face of all this uncertainty. The research literature is of little help, as it appears to lead to a rabbit hole of ever-increasing complexity that leaves one more confused than with answers. The culprit for aggressive post-excavation corrosion – chloride ion – has been known for more than a century (Gilberg 1987; Gilberg and Vivian 2001; Häyhä 1999; Jakobsen 1988; Mardikian et al. 2009; Scott and Eggert 2009: 131), yet we still do not fully understand its interaction with iron nor its behaviour during desalination.

All this can seem disheartening. Desalination appears laborious, hazardous, and uncertain, so why bother? To answer this question, we must understand our expectations and motives.

Iron objects are conserved because we value them. Iron's strength, ductility and prevalence made it an instrumental metal for past cultures. Despite its relatively high susceptibility to corrosion, millions of iron objects have survived buried in the low-oxygen conditions of the soil. They form essential material if we want to understand the cultures that once made, used, and discarded them.

Iron can contribute to this understanding only once it has been excavated. Before excavation, iron can have laid in the ground for decennia; during this time, it has usually come to an equilibrium with its surroundings. Excavation violently breaks this equilibrium and often results in a rapid period of deterioration as the object starts to react to oxygen levels which are far higher in the atmosphere than they are in the ground. (Caple 2000: 108-10; Pye 2001: 23; Watkinson et al. 2013: 409-11).

So, the objects are deteriorating because we have excavated them. This could be seen as an offence towards future generations, as archaeological objects are an unrenewable resource, and excavation is irreversible and destructive. Thus, it is often argued that we should do our best to mitigate the damage we cause by carefully documenting the excavation process and by alleviating the damage excavation causes to the objects as much as possible. This is applying the Brundtland Commission’s definition of sustainability of “meeting the needs of the present without compromising the ability of future generations to meet their own needs” to cultural heritage (De la Torre 2002: 107; Federspiel 2001; Javier 1995).

2.2.Research problem

Research has shown that, despite its shortcomings, desalination is an effective way of controlling post-excavation corrosion. The difference in oxygen-consumption rates between desalinated and untreated material is clear (Watkinson and Rimmer 2013), and condition assessments of previously treated material show that objects desalinated with alkaline solutions survive well in relation to other methods (C. G. Costain 2000; Keene and Orton 1985; Keene 1991; Selwyn and Logan 1993) – let alone in comparison to inaction.

Nevertheless, a survey by Schmutzler that mapped the desalination methods of German conservators in the mid-2000s showed that many conservators were not applying any desalination method to the objects they were treating (Schmutzler 2006). The main reason for this was a lack of time and money. Shortly speaking, desalination was not considered to be worth the effort.

Why is this the case? Surveys of similar nature are not common, so, unfortunately, there is very little data to go from, but the practice has shown that scepticism and methods based on tradition and word-of-mouth are not uncommon (Rimmer et al. 2012: 30; Watkinson et al. 2013: 413). If research data points towards the efficiency of modern desalination treatments, but the conservation field remains sceptical of its benefits, we must look for reasons for this scepticism from beyond the technical details of the research.

2.3.Research overview on the interaction between research and practice

Despite archaeological conservation having deep roots in scientific conservation, it is not devoid of its associated problems. In recent decades, conservation science and scientific conservation have been criticised for failing the expectations set on them. When scientific conservation broke through in the mid-20th century, it was thought that the whole field would soon be revolutionised. More than fifty years later, we can see that the effect of science on conservation has been less dramatic.

This is because of the complicated relationship between science and conservation. The scientific method was introduced relatively late into the conservation field, based on a long tradition of craftsmanship. The scientists employed at the service of the heritage sector often had no experience in conservation, and conservators had no prior experience working with scientists. The two sides struggled to find a common language and understanding.

Some conservators felt that scientific conservation was being imposed on them, ignoring their traditional skills in an invasive manner. In contrast, some conservation scientists were annoyed by their input being ignored by the conservation community (Muñoz Viñas 2005: 117-20). This communication gap led to conservation science becoming detached from the reality of conservation, creating forums where scientists would communicate with each other. This resulted in what Muños Viñas has termed endoscience: science for scientists with no relevance for conservators (2005: 77).

From a desalination point of view, structural studies of archaeological iron and investigations on the mechanisms of post-excavation corrosion count as endoscience. They contribute to understanding the problem but do not directly provide solutions. However, they are necessary precursors to hypotheses about the factors contributing to effective desalination. Their value for the conservation community is realised once the theories they lead to are tested and turned into successful treatments.

This step should be addressed in conservation studies. Conservation laboratories do not have research & development departments responsible for bringing the newest theoretical understanding into action. At the same time, scientists advance their careers more efficiently by publishing further information rather than making previous discoveries more applicable. Thus, we are in a situation where applying current research into practice is not on anybody’s agenda. As Appelbaum has put it:

> “Advancement of knowledge happens on two fronts. At the leading edge is the most advanced knowledge in the field, which may or may not be available to most practitioners. On the trailing end is the rest of us, using primarily what we have been taught, along with information from colleagues or the literature, and from our own experience. Conservation research lives at the front end, but the world of cultural property might well be more efficiently served by spreading around the information that already exists rather than by supporting further research.” (2007: 312)

When papers with a solid practical component are published, they are often quite influential. Especially the German-speaking world has produced many documents that have greatly helped to carry out alkaline desalination in an efficient manner (Greiff and Bach 2000; Rinuy 1979; Rinuy and Schweizer 1982; Schmidt-Ott and Oswald 2006b; Schmutzler and Ebinger-Rist 2008).

However, the phenomenon of practice lagging behind research still beleaguers desalination methodology. We need more studies that fall under the term *technoscience*, coined in a conservation context by Muños Viñas: research carried out to solve specific conservation problems with an engineering mindset (Muñoz Viñas 2005: 144-46).

The critique towards conservation science is often written from a conservation point of view, so it is likely no coincidence that the sharpest critique is directed at conservation scientists, while their point of view is missing from the literature. As sources confirm, there is frustration on both sides. Conservators are often reluctant to apply science in their work, especially if it would mean abandoning methodology they are familiar with for a new approach that studies have shown to be superior:

> "Conservators in many specialities would welcome data on which treatments work best, particularly if it confirms the conclusions they have drawn from years of experience. The question remains, however, as to how many professionals whose customary practices are not supported by new research would change their working method." (Appelbaum 2007: 313)

Conservators are not particularly good at keeping up to date when it comes to the research literature either, perhaps due to a lack of time, money, and relevant studies, but also due to a reluctance to prioritise quality in their work (Muñoz Viñas 2005: 143-44). The complexity of conservation problems is often used to justify disregarding science in conservation practice. It is argued that since every conservation object is unique, the results of scientific studies are irrelevant unless they are performed on the very object at hand. As a result, conservation science is said to "resort to statistics", providing probabilities based on the study of groups of objects rather than definite answers to specific questions (Muñoz Viñas 2005: 122).

However, we must remember that conservation is not alone in its complexity. Most natural phenomena are complex, and science seldom provides definite answers in chemistry or physics, not to mention medicine or biology. The relativity of scientific information should not be used as an argument for ignorance. We can only imagine what average life expectancy would be if doctors from the 1800s onwards had decided to stick to their personal experience and expertise instead of the results of scientific medicine. This is despite not fully understanding how the human body works or why many medical treatments are effective.

Desalination suffers from the complexity described above. As with practically all conservation objects (Muñoz Viñas 2005: 125), each archaeological iron object is unique, as it was impossible to produce two identical objects in the past. The raw material was often heterogenous with lots of impurities, and even mass-production of iron objects in manufactures through smithing and casting would lead to many variations between objects. Once ready, the objects would go through different lives in use, after which they would be discarded and – talking about archaeological objects – would end up underground, where they would start interacting with the burial environment. Underground, even different segments of the same object could face very different conditions, as is often apparent in the state of the excavated material.

All this variation means that every archaeological iron object is an individual, and even different areas of the same object will react differently to a treatment. From the point of view of the chloride ion, a single archaeological nail is a massive, electrochemically active, and complicated structure. Research has shown that chloride is very unevenly distributed deep inside the crevices of corrosion layers, attracted by the anodic sites where iron was actively corroding during burial (Réguer et al. 2007).

Ideally, we would thoroughly investigate each object and carefully extract chlorides from where they are present in harmful concentrations. Practically, it is impossible to distinguish unstable objects from stable ones by other means than waiting for post-excavation corrosion. Mass treatment is the only realistic option that resources in the conservation field currently allow for most institutions.

Since the behaviour of any single object cannot be predicted, the best conservation science can provide is probabilities. This is less than ideal but better than nothing. We, conservators, should ask ourselves what the alternatives are – is basing the treatment on tradition or familiarity with a method likely to provide better results? There is a risk that critique towards conservation science is used as an excuse for conformism.

Muños Viñas calls for adaptive intelligence in conservation work: readiness to deal with unusual, unpredictable behaviours at every moment of the conservation process and adapting to them in real time (2005: 130). Elizabeth Pye calls for reflective practice, which is an elaborated version of the same concept:

> “What is being aimed for in the professional practitioner is known as reflective practice, which is the ability to draw on and use a wide range of different types of knowledge and experience in making judgements and reaching decisions, and it is also the ability to be self-critical (Brockbank and McGill 1998). Effective education is partly ‘about being able and willing to reflect upon what one does and why one does it’ (Ferguson 1992: 413). Reflective practice is what is expected of all professionals whether they are lawyers, architects or conservators.” (Pye 2001: 173)

These ideals set relatively high expectations on conservators. As Ferguson, quoted by Pye, puts it: “To be educated is to be productively ill at ease” (Ferguson 1992: 413; Pye 2001: 172). Most of us would rather stay in our comfort zones. Reflective practice and adaptive intelligence call for active decision-making, and with it come responsibility. With responsibility comes the prospect of critique, and this makes us uneasy. Unsurprisingly, the allure of traditionalism looms over the conservator, especially when there is no external pressure for development.

Too little is written about the psychological factors in conservation, considering how significant a role they are likely to play in decision-making. Appelbaum has written commendably about the conservator’s psyche (Appelbaum 2007), and many a conservator can likely relate to her ideas. Regarding desalination, mainly two cognitive biases play a role in maintaining the gap between current knowledge and current practice: status quo and omission bias.

Status quo bias causes us to prefer the current situation over change. Even when changes would bring about a clear improvement, people disproportionately prefer choices that maintain the current condition. The human mind tends to overestimate unfamiliar risks compared to familiar ones, making changes seem more threatening than they should.

Omission bias, on the other hand, causes people to evaluate committing an action more negatively than omitting it. This means that we are more inclined to feel responsible for the consequences of our actions than our inaction.

From a desalination point of view, laboratories view changes in their desalination protocols with suspicion and are inclined towards sticking to the “business as usual”. It could also lead one to emphasise damage caused by treatment over more significant damage caused by inaction since the first category feels more personal.

These biases should not be confused with healthy scepticism. During the history of archaeological conservation, countless stabilisation methods have been tested with varying degrees of success. Great hopes have been placed on new techniques, but often these have later been found to have been exaggerated. A glimpse at this history will make one approach any new method suspiciously.

However, the degree of consideration of the options distinguishes healthy scepticism from biased thinking. An unbiased evaluation necessitates that all options are considered equally and that no preference is made because of familiarity, tradition, or prejudice.

Currently, there is a significant gap between desalination theory and practice. It can take decades before research results are implemented in the conservation field. This suggests a need for driving forces for development. The conservation field has no institutions responsible for quality-controlling the methodology used by laboratories or keeping individual conservators up to date. There is no conservation equivalent for a "gold standard" used in medicine, and a conservation research & development department is a rarity.

Is this a sign of trust or indifference? Doctor can lose their licence if they do not adhere to good practices because society values human life. In contrast, it would be difficult to imagine any concrete consequences for an archaeological conservator for using an outdated, unsuitable, or harmful methodology. This may imply that society does not care much about the archaeological material's fate.

This gives much freedom to conservators, but with freedom comes responsibility. Since no external forces are demanding professional development, this force has to be internal. Sadly, decreasing funds with constantly increasing numbers of objects will quickly feel overwhelming, and keeping up to date can start to seem like a luxury one cannot afford.

However, effective use of resources necessitates constantly looking for better methodology. Sticking to the same workflow despite a constantly growing treatment queue springs into mind the famous quote: "The definition of insanity is doing the same thing over and over again, expecting a different outcome".

Knowing the pace at which new methodology gets applied in archaeological conservation, the widespread impact of new research lines could be decades away. At the same time, it is necessary to keep treating archaeological iron using traditional methods. There is much to be gained simply by spreading current information and making it easier to apply in practice. To conclude, it seems fitting to quote Muños Viñas:

> ”Conservation needs experts who can convert pure knowledge into useful solutions and make them available to conservators – people who can bring the 'know-that' closer to the 'know-how'." (Muñoz Viñas 2005: 146)

2.4.Desalination research overview

Archaeological conservation stands apart from most other disciplines of conservation in that it does not have as long of a craft tradition behind it (Pye 2001: 37). Archaeological materials usually come out of the ground in a heavily altered condition where they do not behave anything like their pristine counterparts. Thus, it was quickly discovered that craftspeople did not have the skills to address many of the problems specific to archaeological materials, such as rapid post-excavation decomposition of waterlogged organics or chloride-driven corrosion of metals.

This led archaeological conservation to look for answers through scientific means at an early stage compared to other conservation fields (Gilberg and Vivian 2001). It is no coincidence that many of the earliest attempts to apply the scientific method to conservation problems were conducted with archaeological material. Archaeological conservation was scientific before the widespread breakthrough of scientific conservation in the mid-20th century, at least in Northern Europe.

Desalination research has progressed intermittently. In it, one can distinguish the cycle of science that goes from making an observation to forming a hypothesis, conducting an experiment and finally analysing the results, after which the process starts anew. When studying complex phenomena, such as desalination, a single investigation is unlikely to give definitive answers. Instead, repeated cycles will slowly accumulate into a greater understanding of the problem and its solutions. Experiments often do not support previous hypotheses, necessitating a re-evaluation of the theory. This gives the process an arduous "two steps forwards, one step back" character.

A German chemist, Edward Krause, is usually accredited for being the first to name chloride ions as the culprit behind the post-excavation corrosion phenomenon (Krause 1882). He suggested that simple soaking in alternating baths of hot and cold water should be enough to remove the chlorides and that the remaining insoluble compounds should not threaten the object. However, during his lifetime, it was apparent that this was not the case (Jakobsen 1988: 52). Despite this, his observation that the culprit was hiding inside the objects themselves rather than in the air in the form of moisture and oxygen was significant.

The next major step in the desalination research front is the famous publication by Friedrich Rathgen (1898). Rathgen was a German chemist working for the Royal Museums in Berlin. His role in developing conservation research has been so significant that he is sometimes cited as the father of scientific conservation (Gilberg 1987). He noticed the need for a handbook in the field of conservation and compiled the information available at his time into a single work. Many current methods can be traced to this work, even though these 19th-century sources are seldom cited. It should be noted that he mentions desalination by soaking in alkaline solutions – the standard method in use today – as well.

When Rathgen wrote his book, there was a wide discrepancy in the methods used, many of which would be outright rejected by modern conservation professionals. Complete stripping of the corrosion crust in the name of stabilisation was considered acceptable. However, as understanding the information value residing within the corrosion layers was slowly realised, methods based on stripping would gradually go out of fashion (Bertholon 2001).

The next major step was when Harold Plenderleith published another conservator handbook (1956). Plenderleith's work is usually accredited for the widespread popularity of desalination in sodium sesquicarbonate solutions during the mid-20th century. However, we know today that this method is relatively ineffective in removing chlorides.

The decades after Plenderleith are marked by stagnation on the desalination front, and only a little would happen until the significant contribution of Colin Pearson and Neil North. Their publications in the 1970s would mark the starting point of contemporary alkaline desalination methods (North and Pearson 1975, 1978b). North and Pearson argued that chloride extraction is a diffusion-based phenomenon and explained the efficiency of the hydroxide ion compared to other anions. They also established the alkaline sulphite treatment, which would prove highly successful and popular in the coming decades.

However, North and Person suggested that the efficiency of the alkaline sulphite method could be attributed to the reducing properties of the sulphite ion. It was argued that the sulphite ion causes iron oxyhydroxides in the corrosion layers to be reduced to magnetite in the corrosion crust, thus increasing its porosity and promoting diffusion. This was soon questioned, and the method's success was attributed to the sulphite's role as an oxygen scavenger rather than a reducing agent (Gilberg and Seeley 1982).

The method was initially designed to treat marine finds, but it was rather quickly successfully used on terrestrial finds (Rinuy 1979; Rinuy and Schweizer 1980). After an auspicious start, the first reports of the failure of the method started to arrive (Beaudoin et al. 1995). Even though alkaline sulphite treatment could not guarantee stability, it remained popular as it outperformed other treatment alternatives.

Since the alkaline sulphite treatment's efficiency was attributed to the sulphite ion's role as an oxygen scavenger, it was suggested that alkaline solutions deoxygenated by other means should have similar performance. This hypothesis was subsequently tested at Cardiff University, and the results supported the idea (Al-Zahrani 1999; Rimmer 2010; Rimmer et al. 2012; Watkinson and Al-Zahrani 2008). However, another comparative study by Schmutzler (2012) found no significant difference in performance between aerated and deaerated alkaline solutions.

So, currently, there is evidence suggesting that deoxygenated alkaline solutions should outperform aerated ones, but the results are inconclusive. The theory supports the idea, and small-scale testing using real-time monitoring of the desalination process also revealed differences in performance (Kergourlay et al. 2010). However, there is insufficient data to conclude that deaeration significantly affects the treatment. More studies are needed that compare oxygenated and deoxygenated treatments side by side.

When desalination experiments give inconsistent results, it is difficult to determine what causes the differences. Many factors affect the results, and there is no standardised way of testing. This makes it challenging to compare experiments. An in-depth meta-analysis of the studies would be valuable.

Oxygenated or not, it has been shown that all traditional desalination methods can fail in stabilising the treated material. From this point of view, new research lines are essential. The work on subcritical fluids has been going on for more than ten years with very promising results (de Viviesa et al. 2007; Néstor G. González et al. 2013; González-Pereyra et al. 2013; Mardikian et al. 2009; Näsänen et al. 2013; Ternisien et al. 2013). The acquisition cost of the treatment equipment has kept the method out of reach for most laboratories.

However, A-CORROS in Arles, France, has set up Europe's first subcritical treatment chamber (Bayle 2015; Bayle et al. 2016; de Viviés 2022). It is perhaps not a coincidence that a private company took the initiative in the continent, as development – or lack thereof – will directly affect profits, providing a motive for progress. That being said, the first publicly funded subcritical treatment device is being planned at the conservation laboratory of the National Museum in Finland at the time of writing (Arponen et al. 2022).

Another exciting line of research is in Denmark, where reburial in an alkaline waterlogged environment gives promising results (Matthiesen et al. 2022). If the feasibility of this approach can be confirmed, it could be a solution for the Nordic countries, with lots of available bogland. The efficiency of the method could be attributed to the microbial activity in the anoxic bog environment, and in that sense, this line of research intersects with studies made on microbial stabilisation at Haute-Ecole Arc in Switzerland (Comensoli et al. 2017; Comensoli et al. 2019; Joseph et al. 2022).

2.5.Aim

This study aims to make physical deoxygenation of desalination solutions more accessible by testing the feasibility of commercially available vacuum containers as a deoxygenation method. Recent studies have shown that deoxygenating treatment solutions could improve the results of desalination treatment, as removing oxygen from the solution blocks the cathodic reaction path of corrosion, thus releasing chloride ions from their counter-ion role at the anode (Selwyn 2004; Watkinson et al. 2013). This should allow them to diffuse into the treatment solution more freely.

Physical deoxygenation has several benefits compared to chemical deoxygenation. The success of the so-called alkaline sulphite method has been attributed to the use of disodium sulphite, which functions as an oxygen scavenger (Gilberg and Seeley 1982; Rimmer 2010: 69; Schmidt-Ott and Oswald 2006b: 134; Schmutzler and Ebinger-Rist 2008: 251; Schmutzler and Eggert 2010c; Scott and Eggert 2009: 140; Turgoose 1985; Watkinson and Al-Zahrani 2008; Watkinson et al. 2013: 413). Chemical deoxygenation with sulphite increases the environmental load of the treatment and interferes with many chloride analysis methods.

Physical deoxygenation methods do not suffer from these drawbacks. Previous studies have used nitrogen flushing (Al-Zahrani 1999; Rimmer 2010; Rimmer et al. 2012; Watkinson and Al-Zahrani 2008) and laboratory-grade vacuum ovens (Schmutzler 2012) as physical deoxygenation methods, but while effective, these methods are not easy to implement.

Flushing with nitrogen requires a nitrogen supply, which many laboratories lack. A laboratory with no previous experience with nitrogen can also be reluctant to implement it in the current climate, which does not encourage the introduction of another chemical. Also, nitrogen is potentially lethal, replacing oxygen in the air. Even if correct procedures can easily mitigate the risk, the trouble of risk analysis, planning and installation is often enough for laboratories to discard this solution.

On the other hand, laboratory-grade vacuum ovens can be readily found in many institutions. However, they have limited capacity compared to the scale of desalination treatments. Reserving the oven for months to treat a small number of objects at a time is not a feasible option for most institutions.

This is where commercially available vacuum containers step in as a potential solution. Vacuum containers of different types have become increasingly common during the last decades. The uses of said containers range from home cooking and the catering industry to wood impregnation and resin casting hobbyists.

Standard parts for all containers are the main body, lid, gasket, and valve, allowing air to be pumped out with an external vacuum pump. Sizes for containers range from less than one litre to hundreds of litres, so suitable containers are available for most archaeological objects. Being affordable and easily scalable for mass treatment, they present a tempting alternative.

2.6.Research questions

The criteria used to evaluate desalination methods are relative, so the best way to examine desalination in vacuum containers is to judge it against the alternative methods.

A factorial experimental design was chosen for this study. A sample population of archaeological objects were divided into normalised test groups and exposed to selected treatment factors to investigate their effects separately. Three factors were chosen, two of which are binary, while one has three subcategories:

1. Pressure: ambient or vacuum
2. Desalination solution: sodium hydroxide (0.5M NaOH), alkaline sulphite (0.5M NaOH + 0.05 M Na_2SO_3) and RO water.
3. Cleaning: pre-cleaned or not

Evaluating a desalination method is complicated. The goal of conservation treatment is to protect the value of an object, which in the case of archaeological objects, is endangered by the post-excavation corrosion phenomenon. However, defining damage is complex, as many proficient authors exemplify.

The differences between factors must be quantified somehow. In the case of desalination treatments, post-treatment stability is generally considered the single most crucial factor defining success. Stability can be measured directly through oxygen consumption measurements (Matthiesen 2013; Watkinson and Rimmer 2013), but only a few laboratories have the necessary equipment or expertise. That is why residual chloride –remaining in the objects after treatment – has become a standard way of measuring desalination treatment success. Oxygen consumption studies have also shown that it correlates relatively well with post-treatment stability (Watkinson and Rimmer 2013).

Another essential factor to consider is alterations caused by the desalination treatment itself. Damage due to desalination has been reported before, and the risk needs to be evaluated compared to the benefits achieved. Risk management requires information about the severity and prevalence of potential damage. Up to this point, information about damage has been largely anecdotal, with some exceptions.

Treatment efficiency and harmful side effects were essential for treatment evaluation. Residual chloride analysis and condition assessment of the test material before and after treatment were carried out.

The effects of pre-cleaning on the chloride extraction rate were investigated, as there is a discrepancy in methodology between laboratories when it comes to cleaning before desalination. Pre-cleaning should make it easier for the chlorides to be washed out of the corrosion layers as the path they travel gets shorter. Also, it should be easier for the solution to impregnate the thinned-out crust and reach the chlorides. However, there have yet to be studies that would verify these assumptions.

One last feature was tested on all treatment batches towards the end of extraction. Danish desalination tests on objects pre-treated with plasma show that the chloride extraction rate could be significantly enhanced by letting the objects dry between treatment baths (Andersen 2006). This has led some Nordic laboratories to adopt drying as a standard step in their treatment procedures. In this experiment, all batches were dried and re-immersed in fresh solution at the end of the treatment to see whether it facilitated a further release of chlorides.

Other parameters were also measured since they could provide essential insights into the differences between the research factors or spark new questions for the future. To this end, chloride extraction rates, conductivity and pH were regularly measured from all treatment batches. For example, the extraction rate could be a significant factor for many conservators choosing a desalination method.

3. Theory

Conservation, a young discipline dealing with many objects and collections and collaborating with numerous professionals and the public, has struggled to find a common theoretical ground or even a shared definition of the profession. Traditionally, the conservation theory has been understood to deal with these matters and is thus practically synonymous with the philosophy and ethics of conservation (Muñoz Viñas 2005: xii-xiii). The theoretical basis of specific degradation processes or treatments is usually considered as issues separate from the general theory and dealt with on a case-to-case basis.

Conservation objects range from oil paintings to modern art installations, from taxidermised animals to excavated Roman nails and from historical interiors to archaeological sites. Methods and approaches adopted to preserve them are even more numerous. The professionals making the applications are often specialists in their niche fields with a limited understanding of the problems the other disciplines face. It is thus no surprise that finding a theoretical background has proven challenging.

Conservation also suffers from the same ambiguity as any cultural phenomenon. Ultimately, conservation is what we communally agree it to be. Thus, the term can describe many phenomena, and its contents will change. The purpose of language is to make sense of the surroundings to the degree that allows a satisfactory level of mutual understanding. As such, they are not intended to describe the world perfectly rationally, so more often than not, a precise definition of an idea is a line drawn in the water. We should still attempt to come up with a satisfactory definition for conservation.

3.1.Contemporary theory of conservation

3.1.1. What constitutes a conservation object?

Many attempts have been made to define what qualities make a conservation object and to what ends conservation procedures are carried out. In the past, these have often been biased towards specific sections of conservation. One that makes sense for a conservator working with fine arts will likely be rejected by a conservator working with natural scientific samples and vice versa. Thus, a definition that can be generally agreed upon will necessarily be quite broad.

Salvador Muñoz Viñas, one of the most influential contemporary theorists in conservation, defines conservation objects as symbol-bearing objects. According to him, the only thing that connects them is their solid symbolic function, often completely different from the object’s original purpose. Objects created as deliberate symbols, such as modern art or monuments, are exceptions. Another exception is objects he terms ethno-historic evidence. These objects are considered to have scientific value for the ethno-historic sciences of ethnology, anthropology, and history, along with their offspring, including archaeology. (Muñoz Viñas 2005: 22-64).

3.1.2. Why are conservation objects preserved?

The history of conservation objects is connected to the history of collecting, and that history can be traced back to the beginning of human behaviour. Archaeological record contains very early accumulations of objects that escape any practical explanation. It is difficult to see how they would have contributed to the survival of individuals or groups that gathered them. (Pearce 1992: 90-91). Even though we cannot know the motives for such collections of beautiful stones, seashells, stone tools, or other seemingly random objects, it is intuitively easy to relate them to humans’ universal fetishist fascination for beautiful, rare, and wonderful things. This urge to possess and preserve has found countless expressions during history and is also the driving force behind modern collections.

However, we have come far from the curious Stone Age deposits. Collections have become institutionalised into museums which are the main working field for the profession of conservation. The modern museum can be traced back to the Renaissance and its veneration of the antique world, which would become a veneration of the entire human history during the Enlightenment.

Why this happened has been under debate for decades. In the meantime, the heritage sector has kept growing, especially from the 1960s onwards. We are in a situation where the sheer mass of conservation objects is outgrowing the resources allocated to their care. This scarcity has necessitated prioritisation, requiring the conservation sector to critically examine some of its principles and motivations driving preservation efforts.

The modern conservation methodology concentrates on understanding what value makes the object worth preserving and directing the efforts to maintain that value. Not all preserved objects turn into conservation objects; those with symbolic or scientific value for the ethno-historic sciences do. Objects can have such value for countless reasons, for which the conservator must be sensitive when carrying out any intervention.

Many publications aim at guiding the conservator through this evaluation process. Values can be categorised in numerous ways, none of which has established itself. Numerous lists of different categories of values that make objects significant in the eyes of individuals and groups have been compiled. These lists are never all-encompassing, nor are the different divisions compatible. Within the same division, the various categories are not mutually exclusive either. A single object might be preserved for several reasons that change over time. All these systems have in common that they try to make sense of a confusing situation by bringing order – however arbitrarily – into the chaos. It is not easy to give preference to one system over the other.

Values were merited a research project, “Research on the Values of Heritage”, at the Getty Conservation Institute, running between 1998-2005 and producing several reports (Avrami et al. 2000; De la Torre 2002; Mason 1998). One of the stated motives for the research project was the lack of recognised and widely accepted methodologies for assessing cultural values (De la Torre 2002: 3). Two decades later, the situation remains the same, highlighting the issue’s complexity.

As Muñoz Viñas has argued (2005: 180), value, meaning and function are tightly connected concepts that try to describe the motives behind preserving any heritage object in different times and contexts. It could be argued that all terms representing the value of objects are connected similarly.

Caple (2000: 15-17) lists eight different categories of motives for preserving the past that guides the conservation process: curiosity, understanding, control, belief, aesthetics, value, memories, and veneration of age. Coming from the realm of fine arts conservation, Appelbaum (2007: 89-114) has a slightly different list of art value, aesthetic value, historical value, use, research value, educational value, age value, newness value, sentimental value, monetary value, associative value, commemorative value, and age. Pye (2001: 60) presents a shorter list of historic, artistic, scientific, cultural, contextual, condition and economic values, followed by a long list of references for further divisions.

Archaeological objects are usually seen to have value as evidence of the past (Appelbaum 2007: 103; Keene 2002: 17; Muñoz Viñas 2005: 30; Pye 2001: 57), regardless of what name one uses for that value. They have the potential to reveal information about the past, and as source material for study, archaeological collections have more in common with archives than art collections (Keene 2002: 17-19). It has to be stressed, though, that archaeological objects might hold other values (Pye 2001: 57), and one should be careful to respect these as well as possible.

Before conservation work is started, it is necessary to declare to what end it is carried out. Since objects have no values, but humans do, it is essential to turn to people to understand what imputed values one tries to preserve (Appelbaum 2007: 66). This is especially important since conservation treatments, if carried out carelessly, can lessen the value of an object.

3.1.3. From Classical to contemporary theories

The roots of conservation can be found in arts and handcrafts, out of which it gradually emerged (Muñoz Viñas 2005: 1-3; Pye 2001: 43). Before professional conservation, it was natural for artists and artisans to take care of objects since they had craft skills and an understanding for materials. The shift from craft to the conservation profession is marked by adopting conservation-specific principles, methods and ethics (Pye 2001: 34-35), which led to a professional identity by the early 20th century. By then, people working in the field could agree that what they practice fundamentally differed from the earlier activities of servicing, cleaning, maintenance or repairing (Muñoz Viñas 2005: 2). What they could not agree on is precisely how.

The conservation professional's identities are unclear compared to many other fields, and a certain ambiguity regarding professional roles is a characteristic trait of the entire heritage sector. Susan Pearce, referring to Kavanagh (1991), presents a list of features marking the level of professionalism of a field: skills based on theoretical knowledge, the provision of training and education, tests of competence for members, organisation, adherence to a code of conduct, and altruistic service. Talking about curators, she concludes that "[w]hat is clear is that the *idea* of belonging to a profession, modified certainly by discipline loyalties, is important to many curators, however differently they may interpret it as individuals". (Pearce 1992: 122)

Writing specifically about conservation, Elizabeth Pye came to a very similar conclusion in the early 2000s:

> "Conservation is fragmented into a range of different conservation bodies, few of which control their standards of practice. Many have codes of practice, but few have any system for ´policing` them, and few insist on members keeping up to date with their subjects or methods. This fragmentation also means there is no clear voice promoting conservation to the public, so conservation does not apparently behave like a profession." (Pye 2001: 168)

While the theory has progressed in the last two decades, the heritage sector and the conservation field as its part still need to work on essentially the same problems as Pearce and Pye have outlined. As professional identity necessitates adherence to a code of conduct, ambiguity in identity entails ambiguity in theory and ethics.

This confusion about the acceptable means and ends of conservation practice started in the 19th century and has thus lasted well over a century. Until the 1980s, the debate was focused on finding a solid theoretical background that would be universal and rational. The discussion focused on defining the *true nature* of objects (Caple 2000: 62; Muñoz Viñas 2005). If this could be identified, conservation could concentrate on the technical issues of revealing and perpetually maintaining this ideal state. Muñoz Viñas has defined these as classical theories of conservation (Muñoz Viñas 2005: 65-67).

The problem was that the classical theorists could not agree on what the ideal state should be. The plethora of objects and cultures dealing with those objects were too diverse for common ground. The proponents of opposing views would often accuse each other of misunderstanding the nature of the material they are working on and argue for the rational superiority of their opinions. Usually, this did not lead to any conclusion, as logic could not point out a clear winner. Arguments weak and strong could be used to endorse or criticise almost any approach.

Conservation theory has always reflected the general principles and philosophies of their times. The classical debates described above arose from the idealism of the Enlightenment, which emphasised that objective truths are to be established through logic. The truth could not be a question of perspective: for an argument to be considered valid, anybody should be able to adopt it through pure rational thinking. Conservation theorists worked hard to achieve this ideal but struggled to arrive there.

In the spirit of post-modernism, conservation theory finally started to change tracks. From the 1980s onwards, post-modernism introduced the concept of cultural relativism and a critique of positivism and materialism that were soon reflected in conservation theory (Muñoz Viñas 2005: xi-xiii). The quest to find the *true nature* of objects was slowly abandoned, and the problem was reframed.

The meaning and value given to objects were no longer seen as intrinsic qualities but imposed ones. The objects themselves were seen to be dead and mute. In the new contemporary approach, the focus was shifted from the objects themselves to the people endorsing them. These groups are usually called *stakeholders (Muñoz Viñas 2005: 160-63),* and they have taken the place of objects in the theoretical spotlight. Conservation is an activity performed for people, not for objects – the objects have no needs: people do.

The quarter of a century from the 1980s gave rise to many proficient thinkers who integrated the new relativist ideas into conservation theory. Muñoz Viñas has called these writers “semi-contemporary”, drawing the line between classical and contemporary theories where the concept of truth is substituted by the notion of communication (Muñoz Viñas 2005: 153), and *true nature* by meaning as the treatment-guiding criterion.

The semi-contemporary theorists agree that there can be many truths but still exclude the idea of performing a conservation operation that does not pursue *some* form of truth. Contemporary theory lists the pursuit of truth as one possible end but opens the field for the pursuit of meaning that does not necessarily have anything to do with truth. (Muñoz Viñas 2005: 174-76)

This focus on people instead of objects has given rise to the central role of inter-subjectivism in conservation. The contemporary theory states that if objects have no intrinsic value, conservation treatment aims to preserve the value people impose on them. This is a challenging task, as values are equivocal and fickle. Individuals and groups will see the same objects with different eyes, and their views are often conflicting. The meaning of objects will also change over time as cultures develop.

This inter-subjectivism stresses the importance of communication in conservation work. For a conservator to be successful, they need to be sensitive to the needs of the stakeholders and respect their views. Decision-making, which used to be an expert-only zone, has been reframed by Muños Viñas – referring to Sörlin (2001) – as the trading zone, where negotiation, equilibrium, discussion and consensus have substituted traditional authoritarianism (2005: 163-64). Framed this way, the conservator is a mediator rather than a decision-maker (Muñoz Viñas 2005: 156).

3.1.4. Conservation, restoration, or preservation?

One long-standing dispute has got to do with naming the profession. Conservation, as we understand it today, started in Europe, and thus European vocabulary dominates the field. Differences in language resulted in the conservation profession being called restoration in much of Latin and Eastern Europe, while conservator was the established term in Anglo-Saxon countries.

In English, conservation and restoration are separate activities, with or without overlap. Conservation is understood as actions to hinder future degradation of the conservation object while keeping apparent changes in its appearance to a minimum. In restoration, on the other hand, changing the object's appearance is one of the primary purposes for treatment. (Keene 2002: 22-23; Muñoz Viñas 2005: 16-21; Pye 2001: 29)

This difference in names could have to do with the fact that there has been an emphasis on artistic-value-based conservation in the Mediterranean area, while in Northern Europe, more emphasis has been put on scientific value (Muñoz Viñas 2005: 7). One could even see the roots of the division visible in the 19th -century dispute between the approaches of Viollet-le-Duc – a Frenchman – and the Englishman John Ruskin, who have later become symbols of the conservation-restoration dichotomy (Muñoz Viñas 2005: 4-5). Thus, the division has been one of the central disputes in conservation theory from the beginning.

The Anglo-Saxon perspective has dominated the international debate for the last decades. In mainstream English publications, conservation and restoration are understood as opposing ideologies or as two ends of a spectrum of actions. Archaeological conservation is usually seen to be leaning more towards the conservation side (Pye 2001: 29).

Berducou, writing specifically on the treatment of archaeological objects (1996), points out the historical and linguistic reasons behind the problem of defining the term that characterises the conservation profession. The word "restoration" has had several meanings and can still be understood in many ways.

In a narrow, classical sense, it is the actions performed to improve the object's aesthetics: to impose on it the look defined by contemporary ideas of how it *should* be represented. However, Berducou writes that since the word conservator is already used for people responsible for the care of museums and collections in general (perhaps akin to curators in the Anlo-Saxon world), the Latin world has decided to continue using the restorer term by redefining it so that it encompasses the preservation component.

This problem with vocabulary led ICOM to coin the term "conservator-restorer" in 1984. Terming the profession in this way retains the dichotomy between conservation and restoration understood in the classical sense, so it is somewhat problematic. It is a compromise acknowledging that we have no universally approved terminology for the profession, but as such is unlikely to be used in contexts other than those where the Latin and Anlo-Saxon conservation worlds connect. E.C.C.O. also uses the term in their professional guidelines (E.C.C.O. 2002a).

The picture becomes even more complicated when the concept of preservation is pitted against the concept of conservation: are these two different activities, or is there a similarity or overlap between the two, and if there is, then what (Pye 2001: 27)?

When defining conservation, preservation and restoration, one faces many different views, none of which has prevailed over the other. Considering this multivocality, the claim by Muñoz Viñas that "In any reflection upon conservation, even more so in any *theoretical* reflection, the clear and consistent use of terms is a must." (2005: 15), which seems self-evident at first glance, becomes almost hopeless as the discourse loses all coherence if the terms are redefined over and over. However, using the terms intuitively without clear definitions suggests an ambiguity that does not speak well of the level of professionalism in the conservation field.

Muñoz Viñaz decided to use the term *preservation* when describing actions that, according to the classical definitions, would fall within the scope of conservation, and the term *conservation* when the activity encompasses what classical theories would consider restoration or any other related activities. In other words, his definition of conservation in the narrow sense is coined preservation, and in the broad sense, conservation. (Muñoz Viñas 2005: 14-16)

Acknowledging the confusion in terminology, ICOM-CC created a Task Force to establish standard terminology for the conservation profession. The results were published in 2008, and they define conservation as encompassing preventive conservation, remedial conservation and restoration. So, this new definition would suggest that the conservator-restorator term should be abandoned for the simpler conservator.

The ICOM-CC definition for restoration reads as follows:

> "[A]ll actions directly applied to a single and stable item aimed at facilitating its appreciation, understanding and use. These actions are only carried out when the item has lost part of its significance or function through past alteration or deterioration. They are based on respect for the original material. Most often such actions modify the appearance of the item.
>
> Examples of restoration are retouching a painting, reassembling a broken sculpture, reshaping a basket, filling losses on a glass vessel." (ICOM-CC 2008)

3.1.5. *Active and passive conservation*

The practice of conservation is usually divided into active and passive components. When defining these terms, we face the same ambiguity as before, best described by looking at how some prominent authors in the field have approached it.

Caple divides preventive and interventive conservation, the former meaning actions that do not alter the object itself but the environment it is placed in, and the latter at altering the physical and chemical composition of the object (Caple 2000: 37-38). In this division, preventive conservation aims at preventing further decay and damage, while interventive conservation can also be performed to reveal information in the object.

Pye writes along similar lines, differentiating between preventive and remedial conservation by defining preventive conservation as actions aimed at hindering future damage or deterioration. In contrast, remedial conservation seeks to cure the damage that has already occurred (Pye 2001: 29-30). There is a risk for confusion here, as some stabilisation treatments could easily be understood as remedial. Thus, Pye suggests a subdivision into preventive care and preventive treatment to distinguish whether preservation is pursued through control of the environment or treatment of the object.

Appelbaum distinguishes between conservation treatment and preventive conservation without any clear definition of the terms (Appelbaum 2007: 271-72), and finally, Muñoz Viñas draws the line between direct and environmental preservation (2005: 21-25). As stated above, Muñoz Viñas uses the term preservation for activities regularly termed conservation. His division into direct and indirect preservation lies in whether preservation is achieved through intervening with the object itself, such as desalination, or through intervening in the environment the object is in, such as desiccated storage.

ICOM-CC suggests the use of the terms remedial and preventive conservation and defines them as follows:

> "- **Preventive conservation** - all measures and actions aimed at avoiding and minimizing future deterioration or loss. They are carried out within the context or on the surroundings of an item, but more often a group of items, whatever their age and condition. These measures and actions are indirect – they do not interfere with the materials and structures of the items. They do not modify their appearance.
>
> Examples of preventive conservation are appropriate measures and actions for registration, storage, handling, packing and transportation, security, environmental management (light, humidity, pollution and pest control), emergency planning, education of staff, public awareness, legal compliance.
>
> - **Remedial conservation** - all actions directly applied to an item or a group of items aimed at arresting current damaging processes or reinforcing their structure. These actions are only carried out when the items are in such a fragile condition or deteriorating at such a rate, that they could be lost in a relatively short time. These actions sometimes modify the appearance of the items.
>
> Examples of remedial conservation are disinfestation of textiles, desalination of ceramics, de-acidification of paper, dehydration of wet archaeological materials, stabilization of corroded metals, consolidation of mural paintings, removing weeds from mosaics." (ICOM-CC 2008)

3.2.Principles, declarations, and Charters in conservation work

Traditionally, conservation has adhered to several guiding principles established during the 20th century in various declarations and charters. These principles have subsequently been heavily criticised but are still present in conservation work and education alike. They have become too established to be abandoned.

Historically significant are the Athens Charter (ICOMOS 1931), the Venice Charter (ICOMOS 1964), the Burra Charter (A. ICOMOS 1979), and the Nara Document on Authenticity (ICOMOS 1995). In the Nordic countries, the most commonly followed codes are the ICOM Code of Ethics (ICOM 2004) and E.C.C.O. Professional Guidelines (E.C.C.O. 2002a, 2002c, 2002b).

Many of the declarations and principles have been shaped by several factors. Firstly, conservation ethics have their roots in architectural and fine arts conservation, so fundamentals were laid down from their perspectives. Another factor is that they were primarily established during unprecedented economic growth in post World War II Europe. As a result, the principles suppose a high symbolic and economic value of the objects and do not consider financial constraints.

These are different from the realities that most conservators find themselves in these days when the number of heritage objects has been increasing faster than the resources available in the field. Also, the number of conservators working with materials that do not have a high symbolic or aesthetic value has been growing.

These changes are partially to blame for the scrutiny of the classical principles of conservation. A growing number of professionals find them too declamatory to be helpful in their daily work. That being said, when their imperative nature is toned down, the principles are still helpful in guiding conservation decision-making.

3.2.1. Minimal intervention

The principle of minimal intervention dictates that conservation treatment should only change the object as necessary. Here lies the caveat of the principle, since as Caple has put out (Caple 2000: 65), it is not a complete statement. Minimal intervention to achieve what? Minimal intervention becomes useful only once the goal of conservation treatment has been set. Once this is known, actions can be limited to those that serve to reach the stated goal.

As Muñoz Viñas has noted, the principle of minimal intervention frames conservation treatment as sort of a "necessary evil" (Muñoz Viñas 2005: 190): it implies that fundamentally we would like to – and perhaps should – leave the objects as they are, in order not to change their *true nature*.

The truth is that we carry out treatment because we want to cause changes in them. Their current state is deemed unsatisfactory, and the consequences of treatment are considered an improvement. However, defining the desired condition of the object – the *ideal state* using the vocabulary of Appelbaum (2007: 173-95) – is seldom unambiguous, and it is easy to get carried away with the treatment. The principle of minimal intervention is a healthy reminder to keep the target in mind.

The principle of minimal intervention can be found in Article 8 of the E.C.C.O. code of ethics:

> "The conservator-restorer should take into account all aspects of preventive conservation before carrying out physical work on the cultural heritage and should limit the treatment to only that which is necessary." (E.C.C.O. 2002c)

3.2.2. Reversibility

The principle of reversibility means that it should be possible to "undo" all conservation procedures and return the object to the same condition that it was before the treatment. Classical thinking excluded extraneous material, such as dirt or later additions, as their removal was considered acceptable despite being irreversible.

Improvements in analysis equipment have allowed one to investigate objects beyond the naked eye, revealing that almost any added material is practically impossible to remove once it has been introduced. This makes all forms of consolidation, impregnation and coating irreversible procedures. Also, since the ambiguity of the concept of *true nature* has become apparent, it is impossible to objectively discern which materials should be considered extraneous and thus legitimate to remove.

The concept of reversibility merited its own conference in the United Kingdom, which went by the name “Reversibility – does it exist?” held in 1999 (Oddy and Carroll 1999). By that point, it was evident that true reversibility was an ideal that was impossible to achieve in practice. This has led some people to argue that the concept should be abandoned altogether. However, nowadays, the reversibility of treatments is usually assessed on a spectrum, where procedures can be more or less reversible.

The fact that complete reversibility cannot be achieved does not mean we should not consider the reversibility of treatments in decision-making. Whoever has retreated previously conserved material knows that old conservation treatments can significantly affect the expected outcomes of subsequent treatments.

That is why the term *retreatability* has been suggested as a more realistic option for reversibility. It acknowledges that the benefits of treatment can outweigh the undesired consequence of causing irreversible changes in the object. It puts the weight on blocking as few future treatment paths as possible.

The principle of reversibility can be found in Article 9 of the E.C.C.O. code of ethics:

> “The conservator-restorer shall strive to use only products, materials and procedures, which, according to the current level of knowledge, will not harm the cultural heritage, the environment or people.
>
> The action itself and the materials used should not interfere, if at all possible, with any future examination, treatment or analysis. They should also be compatible with the materials of the cultural heritage and be as easily and completely reversible as possible.” (E.C.C.O. 2002c)

3.2.3. Single standard

Single standard suggest that conservators should not prioritise objects above others but stick to a single – high – treatment standard. As such, it relates to the idea of *museum standard*, which also suggests quality, class and privilege.

Early conservation principles were conducted when fine arts conservation had an even more apparent predominance over the other fields of conservation than it currently has. Within this world, the principle of single standard probably was alluring. Suppose the objects have primarily artistic and aesthetic value. In that case, it should not be the conservator’s job to judge whether one work has a higher value over the other but give the same amount of attention and care to each object. Art museums usually have the smallest collections and most extensive resources, so the amount of time and money available per object is relatively high.

In practice, resource scarcity forced conservators to choose between giving a small number of objects with great care or lowering the standards to spread the attention between a larger group of objects. Many conservators silently select the latter option, ignoring the principle of single standard. Nowadays, it is broadly accepted that the amount of attention objects merit is proportional to their overall value (Pye 2001: 33, 158-59). Also, single standard implicitly suggests a similar aesthetic and artistic value for all objects. If such criteria are applied to ethno-historic evidence with low aesthetic and high scientific value, treatment could lower their value.

Appelbaum has redefined single standard from a “one size fits all” approach to treatment to systematicity in values analysis and treatment planning. According to her, single standard does exist, but it exists in applying the same stringent evaluation methodology before treatment. (Appelbaum 2007: 289-94).

Singe standard can be found in Article 7 of the E.C.C.O. code of ethics, though only concerning financial value:

> “The conservator-restorer must work to the highest standards regardless of any opinion of the market value of the cultural heritage. Although circumstances may limit the extent of a conservator-restorer's action, respect for the Code should not be compromised.” (E.C.C.O. 2002c)

3.2.4. Closing comments on terminology and principles

The maze of alternative and often conflicting terminologies and high-flying principles that are impossible to implement in practice quickly exhaust a practising conservator not involved in the theoretical debate (Pye 2001: 35). There is an understandable tendency to fall back to an “I know it when I see it” approach where blurry terminology is used intuitively in daily work. As Suzanne Keene suggests when defining conservation means, “It is often more productive to concentrate on what needs to be done, rather on principles and processes” (2002: 28). This is the practical reality of a lot of conservation work.

Ignoring the theory and focusing on practice can be risky, however. A unified theory and methodology differentiate a craft skill from a profession. Keene might be slightly optimistic in believing that the conservation field has a clear and unified idea about its task and purpose. The impracticality and inconsistency of the current theory risks confusion and moral decay. As Caple puts it:

> “Redefinition of a group's ethical code, whilst it may aid clarity, particularly in a time of change, can jeopardize the uniqueness and permanency of the group's identity. An overlong or elaborate ethical code can become too cumbersome and difficult to use and thus loses the support of the group. Overlong ethical codes may develop as a result of the inclusion of 'good practice' (Oddy 1996) or political ideals (Schemer [sic] 1997) [(Scheiner 1997)] which dilute the strength and reduce the permanence of the ethical code. Some conservators (Oddy 1996) feel that the problems of defining right and wrong, which can vary from one group of conservators to another, creates an 'ethical relativism' (Edson 1997), effectively making the concept of an ethical code for conservation redundant.” (2000: 60)

The fact about conventions, declarations and codes of ethics – one that few practising conservators would be ready to admit – is that their practical impact is generally low. An average conservator in Nordic countries is unlikely to run into a charter or ethical code outside of education. While most institutions are formally committed to one or more, no one monitors whether these principles are practised. Often, a conservator’s only feedback source is their colleagues and peers. Since the principles anyway leave much room for interpretation, strong laboratory-specific subcultures are common.

Many laboratories need more feedback from the stakeholders and management. This absence of feedback is often coined as a sign of trust but could as well be a sign of indifference. If it continues long enough, silence will inevitably lead the conservator to question their work’s significance. This feeling of insignificance fosters cynicism and selfish opportunism: if what one does matters only to oneself, then there is no reason to work towards other than personal ends.

Many conservators feel passionate about objects, though, so the lack of feedback usually turns their attention wholeheartedly towards the objects and collections they work with (Keene 2002: 240). This frequently leads to stagnation since laboratories tend to continue with their established methodology if left unattended (Pye 2001: 160).

Conservation theory has also been beleaguered by a certain rational optimism, focusing more on creating the theory and less on implementing it. A good theory does not automatically lead to good practice, however. It needs to set foot in the laboratories where the work is carried out to have any real meaning, and these laboratories are complex webs of different social groups. Psychological factors have been discussed less than theory, yet they make a difference in daily work (Appelbaum 2007: 266-69, 374-78). Motivation and morals are communal endeavours. If we feel that our work matters to others, we will consider our work important. If we get feedback, we feel that our decisions have meaningful consequences.

Unsurprisingly, virtually every publication on conservation theory and methodology from the 1990s stresses the importance of communication for the conservation profession (Muñoz Viñas 2005: 164, 212). The theoretical grounds for conservation work are blurry, and the field has diversified rather than unified during the last decades. Working in the heritage field, where fighting for authority over limited resources is a daily reality, does not make gathering around a common goal any more straightforward.

The heritage field has been in an almost continuous change for the last decades, and the roles of various professionals are constantly renegotiated in the process. This has led to an air of competition and mistrust among the museum professionals, most of whom are fighting for their established positions and thus view the active role of conservators as threatening, as they fear it might diminish their own space (Keene 2002: 24-28; Pye 2001: 149-65).

Can the conservation field find its voice if contemporary theory paints it as a mediator with no other principles than advocation for the values of others? Who will represent the field if we do not share a common theoretical and ethical setting? We can understand our work in its context only through communication with each other, not through charters and lists of principles.

The actual principles are those which guide daily practice, not those that some board has written down somewhere. The conservation field needs to continue working together to establish these principles. This can only be achieved through continuous communication in an inclusive and respectful atmosphere to avoid dogmatism, and reflective practice (Pye 2001: 173) from professionals in their daily work to resist the allure of conformity.

3.3.Problems with contemporary theory

The contemporary theory of conservation is utilitarian in nature. As Muñoz Viñas puts it: "… it should be pointed out that the best conservation operation is the one that provides the most satisfaction to the most people" (2005: 193). If the role of the conservator is to recognise the stakeholders and the authority that they have on heritage objects according to their contribution to the overall significance of the objects and them being affected by the objects' alteration (Muñoz Viñas 2005: 161), and carrying out the treatment accordingly, then the conservator delegates all responsibility to the public. This is what Muños Viñas warns against as demagogic conservation (2005: 208).

The suggested remedy is the conservator stepping in as a proponent for two special stakeholder groups: academic/specialist users and future users (Muñoz Viñas 2005: 209). The academic/specialist users have already been addressed. Still, the future users' role necessitates conservators to leave the objects open for many symbolic meanings. This *polysemic ability* of objects to convey several messages is inherently valuable in contemporary theory (Muñoz Viñas 2005: 211).

However, if the conservator's role is to mediate a balance between the public, academic/specialist, and future users, then what are the values of the conservator him or herself? This is a problem that Muñoz Viñas acknowledges but avoids as "general ethics" that can be taken for granted (2005: 200) or by appealing to the law by stating that unethical action is illegal (2005: 159).

These statements are not very helpful in any but the most unambiguous situations. History knows many cases in which heritage has been used in ways that we would find appalling. The nazi regime was planning to commemorate the extermination of the Jewish population to emphasise the sacrifices made in the creation of a better world and because the superior Germanic identity would continue to depend on the dichotomy between them and the degenerate Jews (Lowenthal 2015: 544-45).

Had Germany won the second world war, Auschwitz would have become a completely different symbol from what it is today. Nothing in the contemporary theory suggests that it would be immoral for a conservator to work in a museum that portrays the holocaust as the necessary triumph of the strong over the weak if that is the meaning the stakeholders impose on this heritage. I dare claim that most active conservators today would find it difficult to accept such a view.

There are many cases where the popular view differs significantly from the academicians', especially for archaeological materials. Muñoz Viñas prioritises specialist arguments because, through their mediation, the general public can develop an appreciation for the conservation objects (2005: 209). However, in many cases, the public *already appreciates* the material, but in a way that modern study considers obsolete.

What should the conservator do in such a situation? According to contemporary theory, they should seek an equilibrium between the values or functions that objects have for these groups of people, but that would mean promoting meaning posthumously imposed on the material. Muñoz Viñas indirectly acknowledges the problem by writing about the dangers of "democratic radical inter-subjectivism" (2005: 195) and admitting that some stakeholders should be given priority (2005: 210-12). In the end, he also advocates for an active role for conservators:

> "This role, the role of a wise person looking beyond the obvious, is a very important one in conservation decision-making; it is also an extremely challenging one, as it may sometimes be unpopular. As Vestheim et al. have stated, 'conservators must accept the role of being "hindrances" ' when shortsighted decisions are made (Vestheim et al., 2001). When playing this unpleasant role, the experts should keep in mind that conservation is a trading zone, and not a laboratory or a classroom. They should accept the fact that their authority derives from their ability to convince other people: it is for this reason that the need for conservators to improve their communication skills has been highlighted (Leigh et al., 1994; Nordqvist et al., 1997; Frey, 2001; Stoner, 2001)." (Muñoz Viñas 2005: 212)

Let us take the Viking Age as an example. As a concept, the Viking Age emerged during the 19th century out of a period previously known simply as the younger Iron Age. Sweden had suffered a military defeat against tsarist Russia, leading to the annexation of the eastern part of the realm. This was a significant blow to the already weakened empire that had once dominated the Baltic Sea region and much of Northern Europe.

Since the reality of the early 19th century could no longer provide grounds for the military prowess that formed the backbone of national pride, the Swedish nobility turned to the distant past for role models. Soon after the lost war, the Geatish Society was established to promote Nordic culture, which marks the starting point for what has been termed the Viking Revival. Up to that point, the term “Viking” had had exclusively negative connotations of sea raiding and piracy. Still, now it was loaded with ideas of heroism, independence, masculinity, honour and untarnished Germanic legacy. (Frog and Ahola 2014)

It was Erik Gustav Geijer’s poem “Vikingen” that the Viking revival is usually traced back to. Another good example is Esaias Tegnér’s poem “Svea”, where romantic visions of Nordic mythology and nature are directly connected with a vindictive message towards Russia for the conquest of Finland.

The newly created Viking proved an extremely successful concept that would cultivate emerging nationalism. It has also survived through the ages and dominates the popular image of the Nordic Iron Age. Because of its success, the Viking concept has been used to promote countless products, ideas, and cultural movements. Also, Nordic archaeology has dramatically benefited from the Viking story in increased prestige. This creates a moral dilemma for those working in the cultural sector. The Viking concept has greatly benefited the Nordic heritage sector, and nobody wants to slaughter a milking cow, even if they felt that they perhaps should.

The problem is the Viking as we know him is a 19th-century fabulation where national romantic views are imposed on archaeological material. He is not an entirely harmless character either, as he has been – and is – utilised by the far-right, as the acceptance of violence, promotion of masculinity, an assertion of dominance, power, honour, and superiority stemming from untarnished Germanicity is alluring to them (Burke 2018; Kølvraa 2019).

The above example is only one of many where the archaeological material is subject to identity politics and other modern interests. Since these far-right groups clearly contribute to the significance of the objects and will be heavily affected by the objects’ alterations, should we not consider them essential stakeholders for the archaeological material?

According to the contemporary theory, the answer is yes. There is no reason why we should promote a scientific view of the material’s significance over the national romantic lens. If people cannot recognise their preconceptions in how archaeological material is presented, they will feel confused and disappointed, which goes directly against the goal of providing the most satisfaction to most people.

The problem is that most preconceptions are just that and nothing more. We know today that neither Vikings nor cavemen existed in the form they exist in the popular subconsciousness of our culture. Even if we abandoned this story, we would be hard-pressed to find a better alternative since if history has taught us something, it is that we do not know history.

Since the 1980s, there has been an increasing body of literature criticising the heritage industry that promotes using the past to reach modern-day ends. The division between “heritage” and “history”, promoted by David Lowenthal and Michalski (Lowenthal 2015), effectively describes the problem of feeding people’s expectations and the consequences of failing to do so. Scientific archaeology aspires to reach the impossible goal of sticking to “history”, while the general public’s interest is in promoting “heritage”. The gap between these two can be vast in archaeological material, so which should the conservator try to promote? Conservation actions – especially the ones that do not fall into the mundane reality of collections management – are carried out in service of heritage (Muñoz Viñas 2005: 109-13), while one could argue that ethno-historic evidence is taken care of in service of history.

It could be argued that the values of “vision, prudence and humility” that Muñoz Viñas lists as desirable from a conservator (2005: 212) would push us towards promoting history instead of heritage. This listing of guiding values is a short venture from utilitarianism towards virtue ethics. The values that heritage promotes are disappointingly often opposite to what is seen as desirable in a conservator: pride, obstinacy, and chauvinism (Lowenthal 2015). The question is, which path should the conservator emphasise: the promotion of heritage at the expense of values or values at the expense of utilitarianism?

There is no answer to this dilemma since people have had a proprietary attitude towards the past throughout history, and there is no reason why they should stop doing so. Personal memory does not work as an accurate record of past events but to make sense of the present. The same is true of collective memory. For this reason, private and collective pasts are biased and inconsistent. The idea that this is a problem is relatively new and revolutionary.

The merit of the academic study of the past is not only in making the past knowable but in revealing how *little* we know. The role of academics is to be – to borrow an ancient metaphor – the “gadfly of the steed of the public”: a constant reminder that no matter how much we feel that we are familiar with the past, we are not. Admitting the limits of one’s knowledge was a radical idea when it emerged during the Enlightenment. If we let go of this ideal, we return to the times when the past was a free-for-all for anybody to use as they please.

Contemporary acknowledges the universal relevance of the notion “Thou shall not lie”, but more often than not, it is precisely what utilitarian ethics would require of us as heritage professionals. The public wishes to interact with a past that feels familiar, but as the famous quote goes: “The past is a foreign country. They do things differently in there”. If vision, prudence and humility are to be our guiding principles, should we also promote these values in the trading zone?

In a postmodern world, however, it is impossible to impose values on people; the only way to influence them is through communication. The role of the expert no longer relies on a mandate given by the power that resides above the heritage field: kings, emperors or governments. Instead, it ultimately comes from below: from the people that have the final authority in a democratic system. No matter how we look at the matter, heritage experts depend more on the public than the public depends on them:

> “Experts may exert some authority on the laypeople with regard to their field of expertise. But then again, this authority resides in the public recognition of the experts’ ability and good will, and it thus critically depends upon the public perception of the experts’ ability – on the trust that the public is willing to concede to the experts[.]” (Muñoz Viñas 2005: 163-64)

When exposing heritage to academic scrutiny, conservators are in a dangerous position. In a way, they must tell the emperor that he has no clothes while still trying to keep their heads on their shoulders. No wonder that the importance of communication skills is being stressed to an increasing degree (Muñoz Viñas 2005: 164; 212)

3.4.Archaeological conservation from the perspective of contemporary theory

The objects archaeological conservators most work with differ from mainstream conservation objects. As stated above, Muños Viñas defines conservation objects as symbols (Muñoz Viñas 2005: 27-64). However, most archaeological objects are weak symbols. Instead of symbolic value, they are preserved for their scientific value as physical documents testifying of previous times. As the title of Chris Caple's influential book (2006) puts it, they are the "reluctant witnesses of the past". Having "been there", the objects contain information about the histories they have been through.

These kinds of objects are what Muñoz Viñas describes as *ethno-historical evidence* (2005: 59-62). Such collections are often kept out of the spotlight as their scientific value is evident only for those with special competencies. Muñoz Viñas has labelled specialists with such competencies as academic/cultivated users (2005: 209-12). They are the most important stakeholders for ethno-historical evidence, as they mediate between the objects and the public. Experts interpret these materials so that the rest of society develops an appreciation for them. Thus, their contribution is central to the value of the objects. While the interpretations of the past are often politically loaded and subject to intense debate, the preceding interpretation process is an area exclusive to professionals due to its complexity.

This makes the negotiation process for archaeological material – the trading zone, according to the terminology of Sörlin (2001) – a specialised field occupied by archaeologists, curators, collections managers and other museum professionals, and – hopefully – conservators as well. Most other professionals in the heritage field have roots stretching further than those of conservation, so conservators have traditionally found themselves at a disadvantage (Keene 2002: 24-28; Pye 2001: 149-66).

This is not a norm but a general trend and perhaps not an entirely misplaced one. Conservation education is usually aimed at treating objects with a strong symbolic meaning, while problems specific to ethno-historical evidence are given less consideration. This means that the conservator is at risk of being considered incompetent to be a full-fledged member of the trading zone. This is a missed opportunity. Conservators spend a considerable amount of time with the objects and could significantly contribute to interpreting the material they are working on.

Conservation treatment of an object is no less important step of the research process than the excavation preceding it. Indeed, the conservation of an archaeological object is often akin to a micro-excavation of its own and requires a similar mindset and specialist skills (English Heritage 2008). If this is not effectively communicated, then the role of archaeological conservation will easily be reduced to a technical necessity in the minds of other professionals participating in the trading zone.

From this point of view, the idea that the conservator is simply a mediator seeking to balance the views of others is too limited in the context of archaeological conservation. The stakeholders for most archaeological objects are composed of a small group of experts working towards a common goal of preserving the scientific value of the objects and extracting as much information as possible. To work effectively, everybody in the group should understand each other's challenges and capabilities to maximise synergy. In such conditions, territorialism and miscommunication lead to a waste of time and resources.

It should be stressed, though, that while most archaeological objects are conservation objects because of their research value, this by no means excludes other values. Practically no object is valuable for a singular reason, and the conservator should always question their mindset and be open to seeing the conservation objects with different eyes. A routinely carried out values analysis is the safest way to achieve this, though it is seldom carried out in archaeological conservation laboratories with an established workflow. Also, information has little value before it has been effectively communicated to the public. Scientific value is realised once it contributes to our understanding of the past.

3.5.Desalination from a theoretical perspective

Desalination is one corrosion control method that aims to maintain the physical integrity of archaeological collections. It is generally agreed that aggressive chloride-driven corrosion lessens the value of an object, be that aesthetic, scientific or symbolic. An extreme Ruskinian view that we should let these objects fall into ruin is virtually absent. This is perhaps partly because it is the intervention through excavation that exposes these objects to degradation. Thus, it is more difficult to view the process as “natural”. The fact that the objects are subjected to damage because of our actions prompts a feeling of responsibility that encourages preservation efforts.

Desalination is not the only means of corrosion control, however. The process causes irreversible changes in the material – the removal of chloride ions, the desired outcome of the treatment, being one – and this has been seen to go against the principle of minimal intervention. The reported changes range from softening of the corrosion layer to complete disintegration of the objects (North 1987: 222; Selwyn and Logan 1993). Since corrosion layers are a potential source of information, voices have been raised against using any desalination method other than those that use distilled water, especially in Great Britain (Knight 1995; Rimmer and Wang 2010).

Some museums, the Museum of London as the most famous example, have chosen desiccation as their stabilisation strategy. However, drying the objects also results in changes in the corrosion layers, and a survey carried out by Suzanne Keene (1991) gave a very discouraging view of the efficiency of desiccation as a stabilisation method. However, another survey carried out almost twenty years later (Ganiaris et al. 2012) arrived at a very different conclusion, which underlines the difficulties in evaluating treatment outcomes. So much depends on what measure is used for success or failure.

It should also be noted that not all side effects of treatment should be considered “damage”. Some changes are just that – side-effects – with no significant changes to the value of the material. Damage happens when the object decreases in value, and since values are subjective, there is always a subjective factor in play when assessing damage (Appelbaum 2007: 298-99; 363-73; Muñoz Viñas 2005: 101-04).

Especially when it comes to archaeological material, a conservative approach is sometimes suggested that would allow only minimal changes on the material on the notion that the objects contain information that modern methodology cannot reveal (Pye 2001: 25-26, 114-15). This would rule out any change in composition as unethical and limit acceptable conservation methods to environmental control. While rationally justified, this approach is problematic. It does not acknowledge other values besides scientific and emphasises the needs of academic and future users over any other stakeholder group. While the future users should be addressed, we should remember the present users and their needs as well.

According to the terminology suggested by ICOM-CC, desalination counts as remedial conservation (ICOM-CC 2008). Muñoz Viñaz would define it as direct preservation (2005: 21-25), Pye as preventive treatment (2001: 30) and Caple as interventive conservation (2000: 38).

It is usually carried out in connection with other conservation procedures but occasionally in isolation.

Archaeological objects serve as an information source, so their cultural value is in the knowledge we can extract from them. Like all objects, they also have various values implied to them, including aesthetic value (Caple 2000: 29-31). Often these values intertwine so that they become inseparable. For example, objects that retain their form are easier to observe and comprehend, so preserving this form serves the double purpose of maintaining aesthetic and scientific value.

It is widely known that many archaeological iron objects suffer from chloride-driven corrosion, which causes them to shed large portions of their corrosion crusts (Selwyn 2004). If the so-called original surface of the object survives, it survives within the corrosion crust. Thus, this information is lost along with the crust. Examples of objects that have essentially disintegrated are usually relatively easy to find in any significant archaeological collection, and it is not difficult to agree with the interest groups that their cultural value has been dramatically reduced.

Desalination aims at limiting the extent of such damage. This does not automatically make desalination treatment necessary or even desirable. It needs to be weighed against alternative treatment strategies. A world of limited resources necessitates efficiency, and every action comes with an opportunity cost: choosing to do an action always rules out another action (Keene 2002: 52). This can be used as an argument against desalination treatment.

In the Nordic countries, practically all archaeological collections are state-owned and managed with collective funding. The public expects that their tax money is put to practical use, which puts the heritage sector under moral pressure to work efficiently. The global environmental crisis is another factor that necessitates a sustainable use of resources, which often goes hand-in-hand with economic efficiency.

Heritage is often one of the first fields to face cuts in the face of scarcity, as it is seen as a luxury. There is also a hierarchy among collections, where objects with high aesthetic and symbolic value tend to be seen as less expendable than those preserved as ethno-historic evidence. While the public generally appreciates aesthetic and symbolic value, scientific value is less apparent. This is why specialist groups need to communicate scientific value to the public effectively. Archival collections need their proponents. Otherwise, there is a risk of loss due to uninformed decision-making. (Keene 2002: 16-20)

An excellent example of such a situation can be found in Finland, where the head of the National Board of Antiquities questioned the justification of systematically preserving Stone Age quartz flakes if no research is carried out on the material, apparently oblivious to the fact that stone fracture analysis of quartz was one of the internationally acclaimed fields of a study carried out in the country (Kostet 2013; Tallavaara et al. 2010; Vuorio 2013). The comment sparked much controversy in the Finnish heritage sector (Manninen 2014; Mökkönen and Manninen 2013). That the head of such a prominent institution as the Finnish NBA was unaware of the quartz studies highlights the importance of communication. If he did not know these collections' information values, what are the chances that the public would do?

Archaeological iron suffers from a similar mass-material syndrome as Stone Age quartz fragments. For the uninitiated, they appear to be nothing short of random accumulations of rusty lumps, which hardly deserve the amount of care they are currently getting. If this view dominates public opinion, then the academic field needs to communicate the value of the material. This is a serious issue, as it could well result in the material being unnecessarily discarded. This is not to say that it is categorically wrong to discard ethno-historical material. But when such material is discarded, the parties involved in the decision-making should be aware of the values at stake.

In the conservation sector, this has resulted in an emphasis on environmental preservation at the expense of active conservation measures. This argument is also brought up in the context of desalination, where desiccated storage is sometimes advocated instead of desalination. Calling desiccated storage a passive treatment is also misleading since it is a labour- and management-intensive strategy. The desiccated containers need to be regularly monitored and the desiccant renewed (Watkinson and Lewis 2005). If this process is neglected, the material is exposed to renewed corrosion. In extensive collections, managing the microclimate boxes can quickly become overwhelming.

Successful desalination, on the other hand, can relax the required climate conditions, as the iron will start to behave more like historical iron objects. A short period of intensive treatment could thus lead to savings in time and resources in the long run, as the amount of care required to keep the objects stable is significantly reduced. The problem is that this only applies to successful desalination, and we currently have no easy way of knowing how much the stability of an object is improved by treatment.

Desalination, while an effective way of increasing the stability of archaeological iron, does not guarantee immunity to corrosion. On the contrary: archaeological iron will remain sensitive to pollutants and high relative humidities even when successfully desalinated. Oxygen consumption measurements would be one way of investigating how stable objects are post-treatment (Matthiesen 2013; Watkinson and Rimmer 2013), but currently, only some laboratories have access to the necessary equipment and competence.

Finally, one needs to consider that not all iron suffers from aggressive post-excavation corrosion. Ideally, one would only choose the objects that suffer from corrosion for treatment. The problem is that there is no easy way of telling whether the material is chloride-infested or not, other than waiting for the onset of corrosion. This is undesirable for two reasons. Firstly, the corrosion is unlikely to be spotted at its outset. It is more likely that it would have had the chance to develop fully before being detected. Secondly, it has been argued that freshly treated material reacts best to the treatment (Greiff and Bach 2000: 324; Schmutzler and Ebinger-Rist 2008: 251). Again, oxygen consumption measurements could be used to detect unstable iron, but this method needs to become more widely accessible before it is a feasible solution.

Currently, where desalination is carried out, the entire iron material arriving from the excavations is normally desalinated. When older objects are treated, it is not uncommon that the onset of corrosion is the very reason they are chosen for treatment. Desalination is one of the routine procedures carried out in countless conservation laboratories worldwide. From an ethical point of view, this is problematic, as unnecessary treatment should be avoided whenever possible. However, the costs of testing every object before the treatment decision with the current methodology and the potential consequences of delaying the treatment until the visible onset of chloride-driven corrosion justify mass desalination. The methodology should be developed to make a more selective strategy feasible.

A survey by Schmutzler (2006) revealed that when German conservators did not employ desalination, the biggest reason for its omittance was a lack of time and money. This highlights the importance of making methods more accessible to the conservation field, which is beleaguered by a constant lack of resources. Method descriptions and “hands-on” guidance are often very influential and highly respected among conservators (e.g. Greiff and Bach 2000;

Schmidt-Ott and Oswald 2006a, 2006b) even though they do not fetch the same prestige within the academic system.

Desalination is one effective corrosion control strategy for heritage institutions. People who research desalination often advocate its efficiency (Rimmer et al. 2013; Schmutzler 2012; Watkinson et al. 2013; Watkinson and Rimmer 2013), and desalinated objects usually fare well in surveys that are carried out with material treated in various ways (C. Costain and Logan 1985; Keene 1991; Selwyn and Logan 1993).

Ultimately, what corrosion control method will be used depends on the custodians of the objects. Archaeological conservators should therefore keep tight contact with the institution they are carrying out the treatment for and actively provide them with information about the consequences of their policies from a conservation point of view.

3.6.Iron corrosion in soil

Iron corrosion in soil is a complicated phenomenon discussed in detail by numerous sources (Knight 1990; Scott and Eggert 2009: 95-105; Selwyn et al. 1999; Turgoose 1985). From the early 2000s onwards, studies conducted in France have been especially informative in expanding and sharpening our understanding of the structure and corrosion of archaeological iron, initiated by the French nuclear industry aiming to understand better the possible factors affecting the long-term storage of radioactive waste (Neff et al. 2004; Neff et al. 2005; Neff et al. 2006; Réguer et al. 2015; Saheb et al. 2013)

The study of some 40 terrestrial archaeological objects from five French excavation sites helped establish the typical structure of archaeological iron (Neff et al. 2004; Neff et al. 2005). The authors divided the structure into three sections that are, from the innermost to the outermost: the metallic substrate (M), the dense product layer (DPL) and the transformed medium (TM).

The metallic substrate comprises the surviving iron core and its impurities. This represents the unreacted, unaltered matter of the object with slag inclusions and impurities from the reduction stage.

The dense product layer is composed of iron oxides, oxyhydroxides and iron carbonates. This layer is relatively compact, well crystallised and contains unreacted slag inclusions like those observed in the metallic substrate. The main components of the DPL are magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) strips in a goethite (α-$FeO(OH)$) matrix. Depending on the soil composition, calcium carbonate ($CaCO_3$) can also be a significant constituent of the DPL.

Above the dense product layer sits the transformed medium, composed of soil particles trapped in a matrix of precipitated corrosion products. The corrosion products in this layer are poorly crystallised, which contrasts the DPL layer, where good crystallisation can generally be observed. This suggests that corrosion products precipitating in the TM have had little time to crystallise. Iron in the TM is likely composed of iron oxyhydroxides.

On top of these layers, one finds unaltered soil no longer containing corrosion products. The transition from TM to soil can be gradual.

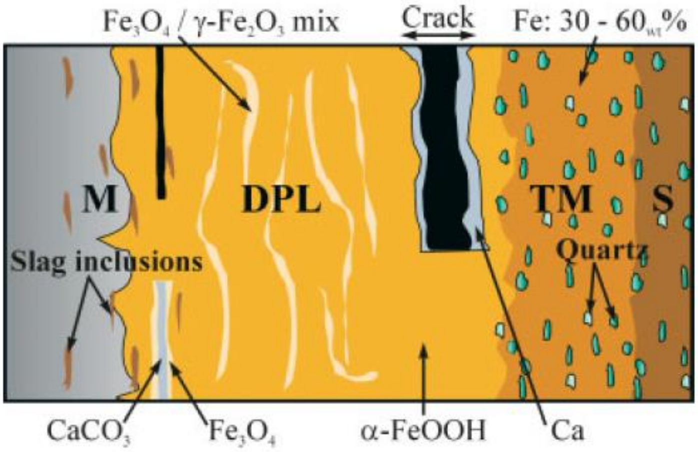


Figure 1: Cross-section of a typical archaeological wrought iron artefact by Neff et al. (2007: 35)

The above applies to most archaeological iron objects under normal conditions. However, numerous exceptions exist, and corrosion forms can differ significantly even within the same object. Objects coming from waterlogged and urban settings often exhibit abnormal morphologies.

Understanding the corrosion processes of archaeological iron is a matter of reverse engineering, as we have not had a chance to monitor first-hand the deterioration that can have stretched over several decennia. The investigations have revealed that iron corrosion in soil is a complicated phenomenon that can vary greatly depending on the soil composition and the local conditions. To make things more complicated, these can change over time, so the conditions recorded on the site today might not be representative of the conditions the object faced when it was recently buried.

Despite these uncertainties, the principles are the same for all iron corrosion. Moisture is practically always present in soil and can readily work as an electrolyte for iron corrosion. The corrosion of iron is an electrochemical phenomenon, and Scott and Eggert (2009: 99) list the fundamental cathodic and anodic reactions as follows:

Equation 3-1

$$Fe \rightarrow Fe^{2+} + 2e^{-}$$

Equation 3-2

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$$

Equation 3-3

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$$

Equation 3-4

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$$

Metallic iron is turned into ferric ions in the anodic reaction at the metal surface. Two electrons are released in the process, the final recipient of which is usually oxygen dissolved in the groundwater. Depending on the soil composition and pH, ferric ions usually undergo further oxidation into ferrous ions, forming iron oxychlorides such as goethite (α-FeO(OH)). This can be a slow process in acidic and oxygenated conditions, meaning that the iron objects from such soils can mineralise completely in – archaeologically speaking – a short timespan (Selwyn et al. 1999).

At the beginning of burial, both anodic and cathodic reactions occur at the metal surface. Still, as the process continues, corrosion products usually start to precipitate on the surface of the iron, passivating it to a certain degree. When such objects are excavated, chloride ions are typically found deep within the corrosion layers at the metal surface, in concentrations exceeding their concentration in groundwater. This led to the theory that the formation of the corrosion crust causes anodic and cathodic reactions to be separated, the anodic reaction, Equation 3-1, still taking place at the metal surface, while the cathodic reactions move to the DPL where oxygen reacts according to Equation 3-2. This separation leads to a positive microcharge building up at the anodic site and causing chloride ions, being a common, mobile anion in soil, to migrate in as counter ions. (Turgoose 1982, 1985)

This model was questioned by investigations by Neff et al. (Neff et al. 2004; Neff et al. 2005) as their studies could not indicate that magnetite and maghemite strips observed inside the DPL would be in touch with the metallic core. Since goethite is practically non-conducive, this would force both anodic and cathodic reactions at the metal surface, and no separation would occur. However, a later study (Réguer et al. 2007: 2740) found evidence supporting the theory of chloride accumulation due to the separation of cathodic and anodic sites, suggesting that the magnetite strips within the DPL could be unevenly in contact with the metallic core, causing localised separation of anodic and cathodic areas.

Chloride is a known catalyst for iron corrosion, but its exact role in the corrosion of archaeological iron has been the subject of some debate. Turgoose believed the role of chloride ions is passive, and it is not directly involved in the corrosion cycle in any way. He stated that chloride does increase the corrosion rate by increasing the conductivity of the solution, but so would any anion. According to him (Turgoose 1982: 98), chloride ions contributed specifically to the deterioration in three ways:

1. They affect the nature of the solid product, e.g. β-FeOOH
2. They aid in the dissolution of iron oxides.
3. They will affect the relative humidity above which an aqueous phase can exist and, hence, corrosion occurs.

Turgoose also provides a formula for the oxidation of iron:

Equation 3-5

$$4Fe^{2+} + O_2 + 6H_2O \rightarrow 4FeOOH + 8H^+$$

Which would explain the acidification associated with anodic sites in archaeological iron.

However, Turgoose's views have been challenged by another model where chloride plays a more active role in the corrosion cycle (Selwyn et al. 1999). In this model, chloride reacts with archaeological iron as hydrochloric acid, acting as a catalyst balancing the reaction. The process was suggested to happen in two stages:

Equation 3-6

$$2Fe + 4HCl + O_2 \rightarrow 2FeCl_2 + 2H_2O$$

Equation 3-7

$$2FeCl_2 + 3H_2O + O_2 \rightarrow 2FeOOH + 4HCl$$

It is worth noting that chloride is not consumed in the process, while iron is turned into oxides.

3.7. Post-excavation corrosion

Post-excavation corrosion is also a complicated process that has been discussed in detail by many prominent authors (Knight 1990; Selwyn 2004; Ståhl et al. 2003; Turgoose 1989). Iron corrosion post-excavation is a complicated process involving numerous steps that differ even within a single object. Only a general overview of the process is provided here.

As long as iron remains buried, access to oxygen remains the limiting factor in the corrosion cycle. If objects survive at all, they are likely buried in an environment where pH, moisture and oxygen concentration allow for the formation of a relatively protective corrosion curst that hinders the diffusion of oxygen at the cathodic sites. Groundwater provides the necessary electrolyte to keep intermediate compounds, such as ferric chloride, in solution, greatly diminishing their occupied volume. Crystallisation within the DPL remains slow and controlled under such circumstances.

This changes when the object is excavated. Oxygen concentrations in the atmosphere are considerably higher than in groundwater, significantly increasing the corrosion rate. Drying leads to delamination and cracking of the corrosion layers (Watkinson and Lewis 2004), which leads to crystallisation inside the corrosion layers. When ferrous salts encounter atmospheric oxygen, they can form voluminous iron oxyhydroxides that cause enormous pressure build-up inside the corrosion crust that can result in disastrous delamination, spalling and cracking of the DPL.

The most famous of these corrosion products is β-oxychloride, known as akaganéite. Akaganéite is formed in conditions with high ferric and chloride concentrations through an intermediate step of Green Rust. Chloride stabilises the hollandite crystal structure of akaganéite, so it is essential for its formation. The formation of akaganéite crystals within the DPL indicates chloride infestation. (Watkinson and Lewis 2011)

Chloride trapped within the crystal structure of akaganéite poses no threat to iron, but chloride can also adhere to its surface. Such adhering chloride can readily contribute to the further decay of iron. Also, there has been a long debate on the long-term stability of akaganéite. Concerns have been raised about its functioning as a “reservoir” of chloride that releases chloride ions into the corrosion layer over time as it is slowly converted to goethite. Current research does not consider this very likely (Watkinson and Lewis 2004).

It is unclear what role akaganéite plays in the corrosion of archaeological iron objects and if it is the problem or merely an indication of the underlying problem of high chloride concentrations. A distinction must be made between post-excavation damage because of spalling and cracking due to crystal formation and continued electrochemical corrosion of iron. The former can occur as objects with high chloride concentrations dry even if no new corrosion takes place. The latter usually requires a high enough relative humidity for the corrosion salts to deliquescence, providing the necessary electrolyte.

Akaganéite has proven notoriously difficult to study, as its synthesis route appears to affect its behaviour significantly (Emmerson et al. 2022). Results achieved with synthetic akaganéite have generally been poorly transferrable to actual archaeological objects. Increasing amounts of interest have been paid to another chloride-containing corrosion product, β-hydroxychloride (β-$Fe_2(OH)_3Cl$) (Reguer et al. 2005). This compound can contain a higher concentration of chlorides than akaganéite but can only survive in conditions where access to oxygen is limited. Thus, it is likely encountered in objects that have been excavated relatively recently. Oxidation of β-hydroxychloride results in the formation of more voluminous chlorinated corrosion products which contribute to the post-excavation deterioration. However, it appears to react well to treatment, possibly explaining why the desalination of freshly excavated objects appears to be more successful.

If chloride concentrations are high enough, ferrous chloride can deliquescence due to air humidity, forming droplets of acidic, brownish solution on the surface of the iron. This phenomenon is known as “weeping iron“: another sign of chloride infestation. (Selwyn et al. 1999).

3.8. Mechanism of chloride extraction

The contemporary theory on the mechanics of chloride extraction can be traced back to North and Pearson (North and Pearson 1975, 1978b), who identified chloride extraction as a diffusion-based process and provided the theoretical framework to evaluate the efficiency of different treatment methods. The theory has been refined (Selwyn et al. 2001), and our understanding of the factors affecting the process has increased, but fundamentally the approach of North and Pearson has stood the test of time.

Desalination can be divided into a series of stages.

1. The diffusion of treatment solution into the corrosion layers
2. Ion exchange between hydroxide and chloride ions
3. diffusion of chloride ions into the treatment solution

Being a diffusion-based process, chloride extraction should greatly benefit from the effect of heat. It has been stated that the process could be sped up tenfold by increasing the treatment temperature to 50 degrees (Schmidt-Ott and Oswald 2006b), but practical testing has not revealed quite that dramatic effect (Guilminot et al. 2012; Kergourlay et al. 2010: 411; Schmutzler et al. 2019).

Besides heat, the process can be sped up by increasing the porosity of the corrosion layers (North and Pearson 1978b; Spiteri and Degrigny 2004: 216). Increasing the porosity makes it easier for the solution to reach the chlorides and for the chlorides to diffuse into the treatment solution. Increasing the porosity of the corrosion layers is a controversial action, however, as any changes in the corrosion layer could be seen detrimental, considering its information value.

Passivating the iron surface releases the chloride ions from their counter-ion role, allowing them to diffuse into the treatment solution more readily (Selwyn 2004; Turgoose 1985). It has been argued that chloride will remain trapped at the anodic sites as long as the iron is corroding. This is usually given as the reason why water-based treatments tend to give inferior results compared to NaOH solutions. The hydroxide ions, in addition to being able to cause an ion exchange with the chloride ions, passivate metallic iron. Blocking the cathodic reaction route will have a similar effect of passivating the iron. Cathodic passivation has the added benefit of not having to reach the anodic sites that can be buried deep within the corrosion layers.

Finally, decreasing the surface tension of the treatment solution and increasing its wettability increases the effectiveness of desalination. Water has a relatively high surface tension and takes a long time to reach the deeper crevices inside the corrosion crust. Sodium hydroxide solutions have a much lower surface tension and greater wettability.

Recent studies have stressed the importance of the treatment solutions’ ability to penetrate the corrosion layers and reach the chlorides as the limiting step of chloride extraction (Selwyn 2004). Potential measurements carried out on objects under treatment have revealed that it can take weeks before alkaline desalination solutions have entirely covered the surface of the metal core – where it is exposed – and it is unclear whether this happens in the objects with the bulkiest corrosion crusts (Hjelm-Hansen et al. 1992; Hjelm-Hansen et al. 1993; Spiteri and Degrigny 2004). The success of the subcritical desalination method has been attributed to the treatment solutions’ greatly enhanced wettability under subcritical conditions and temperature increase that facilitates diffusion and a breakdown of the chloride-containing corrosion products.

4. Experimental setup

4.1.The test factors

It is important to define and isolate the test factors so that their effect is preserved in the noise caused by the inherent heterogeneousness of archaeological iron. The theory of the mechanisms of chloride extraction helps in pinpointing phenomena that could be crucial to the success or failure of desalination. Still, not much can be said about their effect before they are tested in real-life. This is applying the principle of "theory leads, experiment decides" in desalination.

4.1.1. Solution

Many different solutions have been utilised during the history of desalination. Alkaline solutions of sodium hydroxide, with or without the addition of disodium sulphite as an oxygen scavenger, are the current standard. Three solutions were chosen for this test:

1. Sodium hydroxide (NaOH: 0.5 M NaOH)
2. Alkaline sulphite (AS: 0.5 M NaOH + 0.05 M Na_2SO_3)
3. Reverse osmosis water (ROw)

The current theory considers sulphite an oxygen scavenger (Gilberg and Seeley 1982; Rimmer 2010: 69; Schmidt-Ott and Oswald 2006b: 134; Schmutzler and Ebinger-Rist 2008: 251; Scott and Eggert 2009: 140; Turgoose 1985; Watkinson and Al-Zahrani 2008; Watkinson et al. 2013: 413). However, practical testing has shown that sulphite behaves unexpectedly. Schmutzler (2012) found that sulphite had a significant effect on desalination efficiency when used in combination with physical deoxygenation. However, no significant effect could be observed when physical deoxygenation was not used. If the only role of sulphite was that of an oxygen scavenger, we should expect exactly the opposite result.

Al-Zahrani (1999: 137-38) compared the desalination efficiency of deionised water deoxygenated using sulphite with deionised water deoxygenated using nitrogen and found that the latter was more efficient in removing chlorides. The reason for the difference in performance could not be identified, but the author suggested that physical and chemical deoxygenation methods differ.

The sodium hydroxide concentrations in desalination treatments usually range between 0.1 and 0.5 M. A concentration of 0.5 M was chosen as some studies stress the importance of maintaining a high hydroxide ion concentration (Coelho et al. 2014; Pelé et al. 2010; Schmutzler 2012). The original concentration for sulphite (North and Pearson 1975) was 0.5 M, but concentrations as low as 0.05 M were subsequently recommended (Schmidt-Ott and Oswald 2006b) and shown to suffice for the deoxygenation of solutions in closed containers. A concentration of 0.05 M was therefore chosen for this study.

Reverse osmosis water was chosen because it is still used in some institutions. Intensive washing was suggested as a desalination method already by Krause (1882), and since then, an overwhelming amount of evidence supporting water's inefficiency as a desalination solution has accumulated (C. Costain and Logan 1985; Fenn and Foley 1975; Keene 1987: 2-3; 1991; Rimmer et al. 2012; Rinuy and Schweizer 1980; Selwyn and Logan 1993; Watkinson 1980, 1996). Water has exhibited consistently worse extraction efficiencies in comparison to alkaline solutions when boiled, inhibited, deoxygenated and even under subcritical conditions (Drews et al. 2013). The fact that it is still in use testifies to the gap between research and practice.

As a result, modern desalination research seldom tests water as a solution. However, when it has been tested, some interesting results have emerged. Desalination tests on marine iron rivet shavings from the Hunley, a US Civil War era submarine, showed no difference in chloride extraction efficiency between the tested desalination solutions, including deionised water (Drews et al. 2004). However, rivet shavings have a large surface-to-volume ratio, so their behaviour will likely differ from ordinary archaeological objects. Also, all tested solutions left significant amounts of residual chloride in the shavings. Subsequently, subcritical treatment was developed at the Warren-Lasch Conservation Centre, responsible for the preservation of the Hunley, and under subcritical conditions, alkaline solutions showed a higher extraction efficiency.

A desalination test project in Sweden revealed no significant difference in extraction efficiency between deoxygenated deionised water and deoxygenated alkaline solutions, either (Koh and Skogstad 2015). It should be noted that no residual chloride analysis was carried out, the results being evaluated in an accelerated corrosion test. Evaluating treatment outcomes visually after an accelerated corrosion test has been criticised for subjectivity and inaccuracy (Watkinson et al. 2013: 414).

4.1.2. Vacuum

According to theory, deaerated treatment solutions should outperform aerated ones (Selwyn 2004; Watkinson et al. 2013), and studies carried out on real archaeological objects support this view (Al-Zahrani 1999; Rimmer 2010; Rimmer et al. 2012; Watkinson and Al-Zahrani 2008).

Vacuum containers used in this test are intended to limit the treatment solution’s exposure to oxygen rather than to achieve total deoxygenation. There is no data specifying dissolved oxygen levels necessary to passivate chloride-contaminated iron in desalination solutions. More research in the area is needed.

Current theory suggests that the wettability of the solution might be the main limiting factor of desalination. Chlorides can only be extracted in areas that the desalination solution can reach. As iron can have laid in the ground for hundreds of years, chloride ions have had ample time to migrate deep into the cracks and crevices of the corrosion layers. It could take a long time for the treatment solution to reach these areas, if it reaches them at all (Degrigny 2004: 261). Thus, all actions that aid in the process, such as increasing the wettability of the solution or increasing the porosity of the object, should make desalination more efficient (North and Pearson 1978b).

The vacuum could help in impregnating the corrosion crust with a treatment solution. Vacuum chambers are used in resin casting and wood impregnation to remove air trapped inside wood structures or casting moulds, and they could work similarly with archaeological objects. Vacuum is routinely applied in the BTA treatment of archaeological copper objects for the same purpose, for example (Sease 1978: 81).

When the pressure inside the vacuum container drops, the air inside the pores of the corrosion layer expands. The vigorous bubbling of the immersed objects indicates this. Some air will remain trapped in the crevices even when the lowest pressure is reached, but when ambient pressure is introduced once more, the volume occupied by this remaining air shrinks. The treatment solution is consequently drawn deeper into the crevices. A similar pumping action was the motivation behind intensive washing as a desalination method, just caused by temperature rather than pressure.

4.1.3. Pre-cleaning

As stated above, penetration of the solvent into the corrosion layers of the treated objects is likely a major limiting factor in desalination. Removing the bulk of the corrosion crust by mechanical cleaning before treatment should aid extraction. This is why many institutions have chosen to pre-clean the objects before desalination.

This approach has a couple of drawbacks, however. The objects often have to be cleaned again after treatment, which leads to repetition. Also, the corrosion crust could support fragile structures, such as pseudomorphs. Desalination solutions can miscolour silver and copper, so leaving them protected by the corrosion crust for the duration of the treatment could protect them too. It is also worth investigating if pre-cleaning affects the amount of damage caused by desalination.

Object morphology is known to affect treatment outcomes (Rimmer et al. 2012: 37). It seems logical that manipulating the morphology through cleaning should make a difference.

4.2.The test material

Gathering a representative sample for archaeological iron has proven challenging. Variables such as object morphology and chloride content vary considerably from object to object within a single site and even more so on objects from different locations. Therefore, it is difficult, if not impossible, to find sample material so comprehensive that it would represent the entire range of archaeological iron. This is true especially as the conservation field lacks quick, non-destructive, and cost-efficient analysis methods for iron objects that could give some data to predict their behaviour during treatment.

Genuine archaeological material was used in this study instead of artificially created test specimens. All test objects came from an urban excavation in Finland at the centre of Helsinki between August 2018 and January 2019. The excavation took place in the cellar of The Old Customs and Warehouse, built in 1765. The finds could be dated to the 17th and latter half of the 18th century. Large amounts of charcoal and debris were mixed into the layers in the cellar, indicating that they were likely redeposited soil from the surrounding area. The city was burned at the turmoils of the Great Northern War in 1713, and the occupying Russian forces had likely utilised the resulting rubble at the foundation for a fortress built at the site before the Customs House was erected. (Lagerstedt 2020)

Objects from this excavation were good sample material for several reasons. Firstly, the find material was extensive, which resulted in a considerable number of discarded objects. Secondly, most of the finds were likely to originate from the destruction of 1713, after which they had been exposed to relatively similar conditions. And lastly, coming from an urban context, the finds were likely to be infested with chlorides and other contaminants.


Figure 2: Specimen nr. 230 before mechanical cleaning.


Figure 3: Specimen nr. 230 after mechanical cleaning.

The discarded material was picked up from the Finnish Heritage Agency on the 11th of November 2019. The material had been stored in an uncontrolled indoor climate and allowed to dry before delivery. It was put in dry storage (RH < 25%) at the Kiruna Centre for Conservation of Cultural Property on the 13th of November 2019. From then on, the material was kept in dry storage unless it was worked on.

Most discarded objects were nails covered in a thick corrosion crust with soil particles, stones, charcoal, and debris mixed into the crust. Identification of some of these objects took much work as the bulky corrosion products disfigured their shapes. The onset of active corrosion, such as cracking and flaking, was visible on many objects.

The discarded material was too large to be entirely used in the tests, so screening was necessary to form a sample. Choosing a sample randomly without pre-screening could lead to a significant imbalance between test groups, as different objects can have very different ratios between object mass and surface area of the surviving metal core.

The chlorides concentrate on the corroding iron surface, so measuring chloride concentration against metallic iron surface area would be a more meaningful measure of chloride infestation level than measuring chloride concentration against object mass. Ideally, one would want to have the same metallic iron surface area in each test group. Unfortunately, there’s no way to reliably measure this surface area, as the shape of the iron core is irregular.

The screening was begun by measuring the lengths and masses of a sample of 200 nails. Any nails bent over roughly 40 degrees were excluded from the sample. However, as no X-ray was available at this stage, straightness had to be decided based on an evaluation of the distorted form of the objects.

As the objects were fragile and dry, they would lose a fraction of their mass every time they were handled. Dust, fine sand, stones and even pieces containing parts of the original surface of the object would frequently dislodge or flake off. As a result, the object’s weight would be slightly lower with each subsequent measurement.

Once the objects were measured in this way, their mass-to-length ratios were calculated. Mean and standard deviation were calculated for the group and all nails that had this ratio more than one standard deviation from the mean were discarded from the sample. This was done to control bias in the sample due to particularly elongated or bulky objects.

4.3.Documentation

Once the sample was gathered, it was photo-documented and x-rayed. X-ray investigation was carried out using an analogue X-ray cabinet (Hewlett-Packard Faxitron model 43855A, 110 kV, 3:00 min, AGFA Structurix D4 film). X-rays were used to detect and discard objects with no remaining iron core (Figure 4).

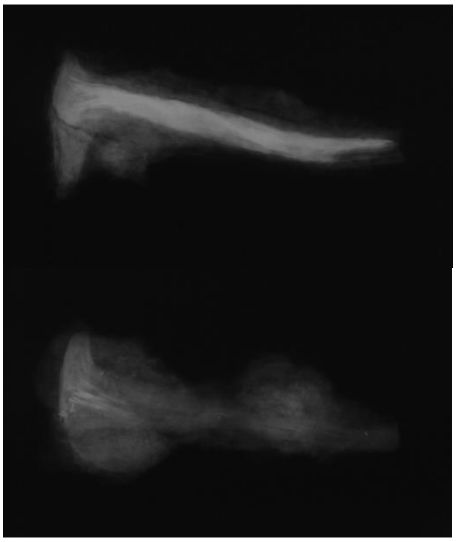


Figure 4: Two X-rayed nails of similar proportions, one (nr. 5) with almost non-existent and one (nr. 9) with substantial remaining iron core. The former was discarded from the sample.

The objects were subsequently photographed after every major treatment step to document the changes these caused in their condition.

4.4.Condition assessment

The prospect of damage due to desalination is a topic that has sparked discussion and worry (Selwyn and Logan 1993). Research literature mentions both desirable and undesirable changes because of desalination, but systematic investigations are uncommon. Probably the most thorough study to date has been carried out by Rimmer (2010). Her conclusion was that the alterations were moderate, with the most fragile material suffering the worst deterioration.

In this study, test specimens that finished their treatment were condition assessed before and after treatment using an edited version of the CARS scale modified for archaeological iron by Ganiaris et al. (2012: 5).

4.5.Division

Out of the nails that filled the sampling criteria described in Chapter 4.2., 128 were chosen to be divided into 16 batches of 8 nails. Since the average weight of nails fulfilling the sampling criteria was about 20 grams, the average weight of each batch was aimed to land as close to 160 grams as possible. The division was done using Microsoft Excel.

Once the 16 batches had been formed, they were divided between the test factors using physical randomisation by drawing from a well-mixed container. The division is visualised in the Table 4-1 below.

Table 4-1

Group	RO-water	AS	NaOH	vac	pre-cleaning
1		x		x	x
2	x			x	x
3	x				x
4			x	x	x
5	x				
6			x		x
7		x			
8			x	x	
9		x		x	
10			x		
11			x	x	
12		x			x
13		x			
14		x		x	
15	x			x	
16			x		

Nails in the batches chosen for pre-cleaning were cleaned using air abrasives. Many objects had fragile fire patina under the corrosion crust, and their cleaning would have been gentler under ordinary circumstances. All objects were cleaned down to the diagnostic surfaces for testing purposes, even at the expense of damage.

After cleaning, the objects were photo-documented, and their weights were recorded. The nails lost roughly half of their weight during cleaning.

4.6.The containers

4.6.1. The vacuum containers

Four different types of vacuum containers were tested for this study.

1. FoodSaver FFC002 Fresh Food Vacuum Storage Container, 475ml.
2. SB Vacuum GN-Container VL0040 | (1/6) | 1,5 L
3. Rieber GN container 1/6 055 with vaculid® lid 1/6 red
4. Vacuum chamber 1.0l, stainless steel VC0918SS by VacuumChambers.eu

FoodSaver containers were tested using a FoodSaver FFS010X vacuum pump, while Lava V.300® Premium pump was used with the GN-containers. Finally, vacuum chambers supplied by VacuumChambers.eu were used with a laboratory vacuum pump, N 816.1.2 KN.18 diaphragm pump by KNF Neuberger.

Figure 5: Stainless-steel vacuum containers by VacuumChambers.eu (VC0918SS) with manual valves, pressure gauges, silicone gaskets and custom-fitted acrylic lids were used in the study.

It was soon discovered that FoodSaver and SB Vacuum GN-Containers were incompatible with alkaline solutions, as they were made of polycarbonate that suffered from stress-corrosion-cracking when loaded in contact with alkaline fluids. This led to leakage and loss of vacuum. FoodSaver containers would also be unreliable and would quickly come to ambient pressure.

Figure 6: Stress-corrosion-cracking caused by pressure and contact with an alkaline solution on a polycarbonate FoodSaver® FFC002 vacuum container.

The use of polycarbonate ruled out options 1. and 2., so a choice was made between options 3. and 4. Having stainless-steel bodies and silicone gaskets, the Rieber GN containers worked well with alkaline solutions, but the stainless-steel chambers supplied by VacuumChambers.eu came equipped with transparent lids, pressure valves and pressure gauges in addition, so they were chosen for testing.

These chambers normally have polycarbonate lids, so they were custom fitted with acrylic lids better suited for alkaline solutions. A single polycarbonate lid was successfully tested outside of the study. The fact that it did not crack could have to do with the flat and thick profile of the lid, but it must be stressed that the time the lid was exposed to an alkaline environment was also relatively short.

4.6.2. The reference containers

Figure 7: PP containers (IKEA 365+, article nr. 705.079.63) used as reference containers in the study.

The IKEA 365+ reference containers (article nr. 705.079.63) chosen for this study came with PP bodies, silicone gaskets and locking lids, as this is what could be expected for an ordinary desalination container in a decently equipped conservation laboratory. They also had the same 1-litre volume as the vacuum containers.

5. Methodology

5.1.Desalination strategy: fixed bath duration or end-point determination

Two approaches are used regarding the desalination bath duration: fixed duration and end-point determination. Fixed duration means that the treatment solution is changed after a set amount of time, for example, every four weeks. In end-point determination, the chloride content of the solution is monitored regularly, and the solution is changed when extraction becomes inefficient.

Both strategies have their pros and cons. Fixed duration usually leads to fewer chloride analyses, as the chloride content is measured only once per solution: from the used solution at the end of each bath. On the other hand, end-point determination typically leads to more measurements but fewer solution changes. When chloride content is measured regularly, each solution can be changed once chlorides are no longer effectively extracted. This strategy avoids unnecessarily discarding a solution while extraction is still underway. A qualitative chloride analysis suffices for a fixed bath duration, but end-point determination calls for a quantitative analysis method.

End-point determination is also a more informative strategy, enabling plotting extraction rate as a function of time. Previous studies have shown that chloride extraction is a diffusion-based phenomenon best monitored this way . As long as there is a significant concentration gradient between the solution inside the pores of the corrosion crust the and free solution, chlorides will be extracted effectively. When this gradient diminishes, diffusion becomes less efficient.

According to North, diffusion remains effective until about 85 % of extractable chlorides are diffused into the treatment solution. Until this point, chloride extraction against the square root of time will be linear (North 1987: 214-15; Spiteri and Degrigny 2004: 319). Once linearity is broken, extraction efficiency can be restored by changing to a fresh solution. Plotting the data from subsequent baths gives the total extraction efficiency across the whole treatment.

Fixed bath duration is less informative in this regard. Since chloride concentration is measured only once, it is impossible to say whether the extraction was still efficient when the solution was changed – and if not, then at what point the solution was saturated.

In both fixed bath duration and end-point determination desalination treatments, the process is considered to be finished once the extraction rate falls to a negligible level. What this level is has been the subject of some discussion and research. North and Pearson, working with heavily contaminated marine finds, suggested that a limit of 20 milligrams of chloride per litre of treatment solution should suffice. Subsequent studies with terrestrial material lowered this limit to 10 milligrams, and the most recent tests have shown that an even lower limit of 5 milligrams per litre results in more stable objects.

As a rule of thumb, the lower the threshold, the more chlorides are extracted and the more stable the objects become. However, overly long treatment times are not necessarily desirable either, not just from the point of view of the time lost and reserved treatment capacity but also because of damage due to treatment. Alkaline solutions cause changes in the corrosion layers, the solubility of siliceous material is greater in an alkaline environment, and the treatment solution attacks organic materials. Thus, limiting the treatment time to the necessary minimum might be best. At the same time, some sources claim that the objects can be safely immersed in the treatment solution for years.

There is one more reason that speaks in favour of limiting the treatment times: lowering of the treatment solution’s pH over time. Hydroxide ions react with carbon dioxide from the air, slowly turning into sodium sesquicarbonate (Pelé et al. 2010; Sullivan et al. 2013). Using sealed treatment vessels alleviates the problem, at least over a period of months.

End-point determination was chosen in this study as it provides a more in-depth view of the extraction process. Chloride concentrations were measured weekly, and once two consecutive measurements deviated from linearity against the square root of time, the solution was changed.

The containers used in the study had a one litre capacity and were filled with eight decilitres of solution. Objects were individually heat-sealed in perforated plastic net to keep any detached pieces linked to the objects.

5.2.Statistical analysis

Statistics are a powerful tool for making decisions in the face of uncertainty. Most natural phenomena are too complicated to be exhaustively characterised, and there is uncertainty in all analysis methods. We cannot, for example, know the exact number, type and distribution of chloride ions in an archaeological object, nor how those ions will react to treatment. Knowing this across all archaeological objects is an even more unachievable goal, so we must accept that we cannot predict how any single object will react to treatment. Instead, we have to work with probabilities derived from a large number of observations.

Statistics help us reveal and quantify patterns in large amounts of data. The human mind is very efficient in making quick decisions based on few observations but is quickly overwhelmed when having to deal with complex phenomena or masses of observations. The brain tends to see patterns where there are none while simultaneously ignoring even apparent trends. Correctly used, statistical analysis can be a great tool in dealing with bias, sorting out significant factors, and making them comprehensible.

Statistical analysis is particularly well suited for studying mass treatment such as desalination. The amount of time and resources available for a single iron object are limited, so desalination is usually carried out for several objects simultaneously. There is no chance to go through a comprehensive testing routine to see how each object reacts to treatment. Hence, testing treatment methods on many objects and choosing the one that performs best on average is a valid approach. Statistics is the right tool for this task.

5.2.1. Basic concepts

Statistical analysis is always carried out on quantitative data: information that can be turned into numbers. Its methodology includes tools to describe and summarise data and make inferences about data we do not have. All data has uncertainty, and acknowledging and quantifying this uncertainty is one of the greatest strengths of statistical analysis. This aids significantly in basing decisions on data in uncertain situations. While statistics do not provide definitive answers to our problem, they can reveal which solution is least likely to be wrong and with what certainty we can claim so. This is called probabilistic reasoning.

The process of statistical analysis usually goes through certain steps:

1. Stating a question we are interested in.
2. Collecting data that helps answer the question.
3. Analysing the data
4. Drawing a conclusion.

For statistical analysis to work, the data collected must be the kind of data that can help us answer our research question. That is why carefully planning the data acquisition process is at least as important as the analysis itself. Statistics relies on gathering limited data from a sample population and inferring the results to the entire population. Usually, the population we are studying is too big to be investigated in its entirety.

In this study, the target population is archaeological iron objects, and it is naturally impossible to include all of them in a desalination experiment. Instead, we have to separate a representative sample from this population. A truly representative sample is one where each member of the population has an equal chance of being included. A sample gathered in this way is known as a simple random sample. Real-life samples are usually biased in multiple ways.

Collecting a representative sample of conservation objects is notoriously tricky, and archaeological iron is no exception. However, conservation is not alone in this problem, as there are many areas where sampling is challenging due to heterogenous populations – not least among human populations. There is enough overlap between the seemingly distant fields of medicine and conservation that analysis methods developed for epidemiology have been successfully applied to archaeological iron material (Keene 1991; Thickett 2022).

Once the sample is gathered and the data acquired, it is time for analysis. The first step is usually summary statistics, where the essential elements of the data are calculated and often visualised using various graphs, tables and plots. The most fundamental values calculated from any dataset are the centre of the data, usually calculated as the mean and the median, and its distribution, represented by variance and standard distribution.

A division between descriptive statistics for the population and the sample is done in statistics. This is to emphasise that we know the true population parameters only in exceptional circumstances, as it is usually impossible to measure the entire population. Instead, the values are derived through measurements from a sample. The sample statistics will always differ from the true population parameters. The size of the difference depends on the size and quality of the sample. The more prominent and more representative the sample, the closer the population parameters will be to the sample parameters.

The sample mean $\overline{x}$ is calculated as the sum of observations divided by the number of observations:

Equation 5-1

$$\overline{x} = \frac{\sum_1^n x_i}{n}$$

Where n = the number of observations¨

The symbol for the population mean is μ.

Mean is heavily affected by outliers, so it is not a very good representative of the centre of data with lots of extreme values. In such a case, the median usually works better. The median is the value that divides the dataset in two: half of the observations are above the median, and half below. If the dataset is composed of an even number of observations, the median is calculated as the average of the two values at the centre of the dataset. The median is not affected by outliers, so it is a good representative of the centre of data with lots of extreme values.

In evenly distributed data, the mean and median are the same. However, this is usually not the case in limited datasets based on real-life observations. Outliers push the mean of a dataset apart from the median, known as the skewness of the data. The greater the distance between these two values, the more skewed the dataset. If the mean is greater than the median, the data is positively skewed. If the mean is less than the median, the data is said to be negatively skewed.

Once the centre of the dataset has been determined, it is good to see how tightly the data is clustered around the centre. Variance is commonly used to measure how spread the data is: it is a measure of dispersion. Variance is calculated by dividing the sum of the square of each observation from the mean by the number of observations minus one (the mean has no deviation from itself):

Equation 5-2

$$s^2 = \frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1}$$

The problem with variance is that it operates in squared units, so it has different units than the original data. That is why the square root of variance, known as standard deviation, is often used to measure dispersion. Standard deviation operates with the same units as the original data, so it is easier to comprehend:

Equation 5-3

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1}}$$

Before going any further from summary statistics, it should be checked whether the data fulfils the four basic statistical assumptions:

1. Linearity.
2. Independence of data.
3. Symmetric (normal) distribution. A normally distributed dataset is symmetrical about the mean, so the mean and median are identical. When such a dataset is visualised, most values cluster around the centre, tapering off as distance increases. Because of its shape, the data is said to follow a bell curve, also known as Gaussian distribution.
4. Same variance across groups.

These four criteria should be fulfilled for most statistical analysis methods to be valid. In real life, the data seldom fully comply with them. Care has to be taken when such data is analysed, as there is a risk of false conclusions.

5.2.2. Statistical significance: p-value and α-level.

The results of a study are statistically significant when it is improbable that the observed outcome could be explained by random chance. To check this, it is necessary to state a null hypothesis, H^0, that one tries to reject with the help of data. We reject the null hypothesis only when there is strong evidence favouring an alternative hypothesis, H^A.

In the case of this study, the null hypothesis is that none of the test factors affects treatment outcomes. We assume that any observed differences are coincidental and accept the alternative hypothesis – that one or several of the test factors has a significant effect – only if there is a low probability of achieving the observed results by change.

To understand how this is examined with the help of statistics, we have first to define some basic concepts of probability.

Experiment: an action whose outcome is uncertain.
Sample space: a set of all possible outcomes of an experiment.
Event: a collection of outcomes of an experiment.
Probability: a rule assigning each event a value on [0,1] reflecting the chances of the event occurring.

This leads us to the three axioms of probability:

1. For any event A, $1 \leq P(A) \geq 0$.
2. If S is the sample space, $P(S) = 1$, and $P(Ø) = 0$, $P(Ø)$ symbolising a so-called "empty set" or no observation. This means that the sample set encompasses all possible outcomes of the experiment, and no outcome exists outside of it.
3. Events are mutually exclusive.

The probability of achieving the outcome of the study, assuming that the null hypothesis is true, is represented by the *p*-value. The *p*-value can be turned into a percentual probability by multiplying it by a hundred. For example, a *p*-value of 0.1 means a 10 % chance of achieving the observed result by chance.

The p-value is relative and does not indicate significance by itself. For that, some threshold must be agreed upon, and this is the role of the so-called level of significance or α-level. The level of significance is the arbitrarily chosen threshold that the p-value must fall under for the results to be considered significant. The level of significance could theoretically be anything between 1 and 0, but practically it usually lies between 0.1 and 0.01, 0.05 having become something of a standard. A low α-level is favoured when the consequences of a false conclusion could be severe. Reaching a low α-level usually means using large sample sizes and much data. A more relaxed, wider α-level can be used when the positive impact of arriving at a conclusion outweighs the possible negative consequences of an erroneous decision.

A significance level of 0.05 is also used in this study. It is important to remember what these numbers signify to avoid getting carried away by them. A statistically significant result does not guarantee that the conclusion is correct. If we conclude with a p-value of 0.05 a hundred times, statistically speaking, five of those conclusions are erroneous. Similarly, a result with a p-value of 0.2 is not considered statistically significant but could still indicate that the null hypothesis might not hold true. In such a case, there is not enough evidence to confidently draw a conclusion, but at the very least, the question deserves further investigation. For example, a larger sample group could push the p-value below the α-level.

5.2.3. Factorial design

A study investigating the effects of multiple factors can be effectively conducted using the so-called factorial design. In a factorial design, the sample group is divided into subgroups, and the treatment factors are equally and randomly divided between the subgroups.

The factorial design in this study has three factors, two of which are binary, and one has three levels:

1. Solution type: NaOH, AS and ROw.
2. Pressure: ambient or partial vacuum.
3. Cleaning stage: pre-cleaned or non-pre-cleaned.

The division of the test material between these factors has been discussed in Chapter 4.5. In a sense, the design can be likened to a 2^k factorial design, except that one of the factors has three instead of two levels, leading to a minimum of 12 instead of 8 groups. The total number of 16 groups in the study is explained by the duplication of groups that non-pre-cleaned NaOH and AS groups, which were considered the most interesting before the study.

5.2.4. ANOVA

ANOVA is an abbreviation of ANalysis Of VAriance. It is an efficient analysis method to investigate whether categorical variables have a significant effect. ANOVA breaks down the variation into component parts and then examines their significance.

ANOVA is used to investigate the effects of one or more explaining or predicting variables on a response variable. The explaining variables are categorical, while the response variable is continuous.

ANOVA test compares the variation between groups to the variation within groups. If the grouping significantly affects the response variable, then variation between the groups should be greater than variation within the groups.

The null hypothesis of an ANOVA test is always that any differences in group means are random, and categories have no effect on them, while the alternative hypothesis is that categories indeed have a significant effect:

H_0: the mean outcome is the same for all categories.

H_A: the mean of the outcome is different for some or all groups

The null hypothesis is rejected if analysis reveals strong evidence against it. This is achieved by measuring different sources of variance in the data and then comparing their relative sizes.

There are two primary sources of variation to consider. The first one is the variation between groups. This is calculated by taking the squared sum of each group's mean's deviation from the overall mean, weighted by the sample size of the group. We call this the sum of squares between (SS_B):

Equation 5-4

$$SS_B = \sum_{1}^{n} n_{group} \, (\overline{X}_{group} - \overline{X})^2$$

The next one to consider is the source of variation within groups. This is calculated by looking at each value's difference from its group's mean. We call this the sum of squares within (SS_W):

Equation 5-5

$$SS_W = \sum_{1}^{n} \left(X_i - \overline{X_i}\right)^2$$

If the difference between groups is not that big, then the sum of squares between and the sum of squares within will be close to each other. When there is a difference between the groups, the sum of squares between and the sum of squares within will also be further apart. In other words, the difference in these sums reflects the difference between the groups.

Finally, there's the sum of squares total (SS_T), which is the squares sum of all observations from the overall group mean:

Equation 5-6

$$SS_T = \sum_{1}^{n} \left(X_i - \overline{X}\right)^2$$

Using the sum of squares within, it is possible to calculate the within-group variations (MSW):

Equation 5-7

$$\frac{SS_W}{N-k} = MSW$$

Where N=total sample size and k=the number of groups.

We also look at the variation between groups (MSB):

Equation 5-8

$$\frac{SS_B}{k-1} = MSB$$

Where k=number of groups

Using the within and between group variations, it is possible to calculate the F statistics, also known as the F ratio:

Equation 5-9

$$\frac{MSB}{MSW} = F$$

In other words, F is the between-group variation divided by the within-group variation. If these values are close to each other, then $F \approx 1$ and we fail to reject the null hypothesis. If $F >> 1$, then between-group variation is greater than within-group variation, and we reject the null hypothesis.

However, the F ratio alone does not tell whether any observed difference is significant. This is calculated using a sum of squared standard deviates, known as chi-squared distribution: χ^2.

Equation 5-10

$$chi - squared\ distribution\ \chi^2 = \frac{sample\ variance}{population\ variance}(degrees\ of\ freedom)$$

Chi-squared distribution allows for the calculation of F-distribution, which is formed by taking the quotient of two independent chi-squared distributions, divided by their degrees of freedom:

Equation 5-11

$$Fdistribution = \frac{\left(\frac{\chi^2 numerator}{df\ numerator}\right)}{\left(\frac{\chi^2 denominator}{df\ denominator}\right)}$$

Significance is evaluated by comparing the resulting F distribution with the F ratio. A p-value less than our α level means we reject the null hypothesis of equal means.

It was necessary to test whether the data complied with the conditions of the ANOVA test. Levene’s test of equality of variances was used to test for the equal distribution of variances between the different factors. Normality was tested using Shapiro-Wilk and Kolmogorov-Smirnov tests.

A few phenomena emerged during the testing that motivated repeating the ANOVA test with different parameters. One of these was the weights of the nails, which differed significantly between the pre-cleaned and non-pre-cleaned specimens. The problem of measuring residual chloride concentration against mass becomes especially apparent when comparing pre-cleaned and non-pre-cleaned objects.

The surface area of the surviving iron core is arguably the best value the residual chloride amount could be compared against. The surface area could be calculated using computed tomography. Still, the equipment and skills necessary to do so are not generally accessible in the cultural heritage sector.

Cleaning does not affect the surface area of the object’s remaining iron core. However, it strongly affects weight. It was thus assumed that there is a smaller deviation in the weight-to-surface area relation when uncleaned weights are used for the entire sample, including the pre-cleaned specimens. That cleaning did not appear to lead to a significant reduction in chloride content supports the validity of this approach. Thus, the residual chloride ANOVA test was repeated using weights before cleaning.

A comparison between untreated pre-cleaned and non-pre-cleaned objects can be used to exemplify the difference. Objects would lose about half of their weight in pre-cleaning on average, but despite this, they contained about 25 % more chloride than the uncleaned ones. Considering the significant differences in the chloride contents of the test objects, this result does not say more than that the amounts of chloride removed during cleaning were not substantial. This is in line with the theory that most chlorides are situated deep within the corrosion layers, next to the surface of the iron core.

The Shapiro-Wilk and Kolmgorov-Smirinov tests indicated that the residual chloride data are not normally distributed, thus violating one of the basic requirements for ANOVA testing. There is a strong correlation between sample size and how well the data follows the normal distribution. However, whether the residual chloride data would follow the normal distribution in larger samples must be tested in practice.

The residual chloride data are positively skewed, with the bulk of the chloride measurements at the lower end of the scale and a long tail of outliers with larger residual chloride amounts. These are typical qualities of the log-normal or Galton distribution. The log-normal distribution is a continuous probability distribution whose logarithm is normally distributed.

To test whether the data follows the log-normal distribution, it was log-transformed by taking the natural logarithm of the results. The ANOVA test was repeated using the transformed data to see if it made a difference in the results.

5.3.Acid digestion

Digestion in both nitric and sulphuric acid was attempted. The aim was complete digestion of the specimens. This ensured that all residual chloride was included in the resulting solution. First, it was tested whether digestion in acid was feasible by selecting groups of samples to be digested without desalination treatment. Tests were carried out in LDPE bottles with screwtops. Digestion was carried out at room temperature.

Groups 24 and 26 were chosen to be digested in nitric acid, while groups 20 and 22 were selected to be treated using sulphuric acid. Groups 22 and 24 were chosen for pre-cleaning before digestion, while groups 20 and 26 were treated as they were. The groups were randomly assigned.

5.3.1. Digestion in nitric acid

Nitric acid was prepared individually for each test specimen by mixing 25 ml of 65 % nitric acid in 100 ml of RO water. The concentration of the resulting solution was approximately 3.6 M. Dilute nitric acid reacts with iron, producing iron(III)nitrate, nitrous oxide and water according to the formula:

Equation 5-12

$$4Fe_s + 10HNO_{3(aq)} \rightarrow 4Fe(NO_3)_{2(aq)} + N_2O_{(g)} + 5H_2O_{(l)}$$

The reaction is slow and nitric acid is consumed in it. Digestion was done in a fume hood with the necessary precautions considering that nitric acid is toxic and corrosive.

The reaction between the test specimens and the nitric acid started slowly but was speeded up as the exothermic reaction warmed up the digestion solution. Some specimens foamed, releasing greenish-yellow gas easily seen with the naked eye. Testing the pH with a piece of pH paper dipped in RO water showed a value of ca. 1.5. Sensory testing revealed a strong smell of chlorine. When possible, the screw-tops of the LDPE bottles were put on lightly to hinder evaporation while keeping overpressure from building up. Where the reaction was strong, this was out of the question, however. A cold-water bath was used to cool down the samples when they would heat up excessively.

This raised concerns about the loss of chlorides as nitrosyl chloride (Schmutzler and Eggert 2010a). If chloride is lost from the sample in gaseous form, its concentration will be underestimated in the analysis. Nitric acid did not perform very well as a digesting agent either, as after an aggressive start, the digestion process was prolonged, the inner corrosion layers (DPL) being tough to digest.

The reaction would be significantly slowed during the subsequent weeks, and the resulting solutions were thick with gel-like undigested mass and DPL particles. After initial digestion in the bottles, the specimens had to be transferred to 250 to 500 ml Erlenmeyer flasks covered with laboratory film with a needle hole to keep pressure from building up inside the flasks while still hindering the evaporation of possible volatile compounds. RO water and acid had to be added to the solutions to keep the digestion process going.

Many nitric acid digestion samples contained significant amounts of undigested material, mainly from the TM and DPL layers, even after a prolonged digestion period and several acid additions. The resulting solution took time to work with, filter, and analyse.

5.3.2. Digestion in sulphuric acid

Digestion was tested using 100 ml of 3 M sulphuric acid per specimen. Sulphuric acid reacts with metallic iron, forming iron(II)sulphate and hydrogen:

Equation 5-13

$$Fe_{(s)} + H_2SO_{4(aq)} \rightarrow FeSO_{4(aq)} + H_{2(g)}$$

Sulphuric acid is consumed in the reaction. Digestion was carried out in a fume hood with the necessary precautions considering that sulphuric acid is corrosive.

The reaction between sulphuric acid and the specimens was less aggressive than that between nitric acid and the specimens. It was still an exothermic reaction resulting in the release of hydrogen gas. The caps of the LDPE bottles were kept lightly screwed on to hinder the evaporation of volatile compounds while keeping overpressure from building up inside the bottles. A cold-water bath was used to cool down the samples when they were heating up excessively.

Figure 8: A specimen fully digested in sulphuric acid. Notice the bluish-green colour, the dark undigested material, and the layer of crystalline ferrous sulphate at the bottom of the LDPE bottle.

The gas formed during digestion in sulphuric acid was odourless and colourless. There were no detectable signs of losing chlorides as volatile compounds, though the possibility cannot be ruled out. Loss of chlorides as volatile hydrogen chloride due to excessive sulphuric acid has been reported (Schmutzler and Eggert 2010a).

Digestion was faster and more complete in sulphuric acid than it had been in nitric acid. Generally, the resulting solutions were more transparent, less staining and easier to work with. However, the sulphuric acid samples had to be moved to 250 or 500 ml Erlenmeyer flasks to finish the digestion process. As can be seen in Figure 5, clear bluish-green crystals formed inside the flasks after some time, suggesting that the solution was becoming saturated with iron(II)sulphate. Moving the sample into a bigger container and adding RO water led to the dissolution of the crystals and a continuation of the digestion process. Acid was added when the digestion rate became negligible despite a crystal-free solution.

Sulphuric acid would completely digest metallic iron and DPL, resulting in a clear bluish-green solution with few residues. However, samples with thick corrosion layers could show significant amounts of undigested material, a dark colour, and a muddy texture.

5.3.3. Conclusion of the digestion testing

Sulphuric acid was chosen over nitric acid as the digesting agent. Digestion in sulphuric acid was faster and more thorough and resulted in a solution that was easier to work with. The initial reaction was also less aggressive than what was observed with nitric acid.

5.3.4. Digestion sample preparation for chloride analysis

The ISE electrodes used for the residual chloride analysis set the conditions for residual chloride samples. The optimal pH range for chloride ISEs used in this study was 1 to 12. The sample pH was generally < 1 after digestion, so it had to be adjusted before measurement. This was done using solid NaOH pellets. The pellets were gradually added to the samples and allowed to dissolve while the pH was regularly monitored using pH paper. The target pH was above 1, as it was desirable to keep the samples as acidic as possible to keep iron hydroxide from precipitating. Chloride can adhere to freshly formed iron hydroxide, leading to an underestimation of chloride concentration in subsequent analysis (Schmutzler and Eggert 2010a). It was discovered that precipitants could start developing at surprisingly low pH levels (> 2), probably due to the high ionic concentrations of the solutions. If this was observed, pure sulphuric acid was added dropwise until the precipitants dissolved, after which the pH was rechecked.

It was discovered that the NaOH pellets used for pH adjustment contained enough chloride to interfere with the residual chloride analysis. Two different batches of pellets were used, and their chloride contents were analysed experimentally by dissolving 20 g NaOH in ROw and neutralizing the solution using 65 % HNO_3. The resulting solution was spiked with a known amount of chloride and compared to a RO water reference solution spiked similarly.

The difference in chloride concentration was determined using Sherwood Scientific Model 926 chloridometer. Because of the low concentrations, each sample was measured seven times and calculations were based on averages.

The analysis revealed that the NaOH batches used in the study contained 40 ± 10 mg/kg and 50 ± 10 mg/kg chloride, despite being analytical grade reagents.

The result allowed one to subtract the chloride introduced by neutralization from residual chloride calculations. However, it introduced another source of error to the calculations, and it would have been preferable to use sodium hydroxide with a lower chloride content. The error is proportionally greatest in samples with low residual chloride concentrations. The problem was further exacerbated by the fact that the exact amount of chloride used in neutralization was not originally recorded, as the high chloride concentration was discovered in the middle of the analysis process. For these samples, the added chloride amount had to be estimated by using average values calculated from subsequent samples, which naturally increased the uncertainty of the residual chloride concentrations.

Figure 9: a residual chloride sample ready for analysis. Notice the green colour, and the layer of rust-brown precipitate at the bottom of the measuring glass, formed after filtration.

Measurement with ISEs also necessitated that the samples be free of solids, so filtration was necessary. This was first carried out using simple glass funnels, but the high viscosity and solid content of some samples – especially those that had not gone through pre-cleaning – meant that filtration this way could last days. The glass funnel and the receiving measuring glass were covered with laboratory film perforated with a needle to keep the filtration process from stopping because of air pressure. Once filtration was done, the filter paper was flushed with RO water to get as much chloride into the filtrated sample as possible.

It was soon discovered that this method was not viable, as filtration took too much time. The majority of samples were thus filtrated with a Buchner funnel. Even with a vacuum, the filtration could still take over eight hours for some samples. Two different types of filter paper were used, VWR Type 413 and Type 417, depending on the amount of undissolved solids in the solution. Some solutions were filtered twice, but as this did not appear to bring any benefits compared to single filtration, most solutions were filtered once.

An example of a filtered sample can be seen in Figure 6. The colour and consistency of the filtered solution varied from light green to deep brown, pre-cleaned samples resulting in more transparent solutions. At times, rust-coloured precipitates could form after filtration. This raised concerns whether the samples were electrochemically stable, as ISE measurements require.

As stated before, there is no standardised methodology for residual chloride sample preparation and analysis. This is a crucial step in desalination studies and more information is needed about good practice in chloride analysis (Schmutzler and Eggert 2010a). A commendable effort has been made by Roche et al. (2022), but their publication was unfortunately not available at the time residual chloride analysis was carried out in this study. Also, it their method has not yet been tested with real archaeological objects.

5.3.5. Testing residual chloride analysis using standard solutions

Tests with self-mixed standard solutions were carried out to validate the analysis method for residual chloride. Concerns have been raised about the possibility of losing chloride from acid-digested samples as volatile chloride gases (Schmutzler and Eggert 2010a).

Two different standards were mixed to investigate how much chloride was lost during digestion. Chloride was added to sample A before digestion, while the same amount of chloride was added to sample B after digestion. If chloride had been lost during digestion, this would have been revealed in the differences in chloride concentration between the two standards.

Both samples were prepared by digesting 20 grams of metallic iron powder with 100 ml of 4 M sulphuric acid. Chloride was introduced by adding 25 ml of 1000 mg/L chloride standard solution directly at the beginning of the digestion into sample A and at the end of the digestion into sample B.

Standards were mixed in a fume hood using the necessary precautions considering that the reaction between iron powder and sulphuric acid can be violent. Acid was added in increments, and a generous cold-water bath was kept at hand. Mixing was carried out in 100 ml LDPE bottles to simulate digestion conditions. The bottles were capped loosely to keep potential volatile chlorides from escaping freely. However, the caps had to be loosely attached to let the hydrogen formed in the digestion process escape.

It was soon discovered that the volume of the solution was not enough for the forming iron sulphate to dissolve. Bluish-green crystals precipitated in the bottles, indicating that iron sulphate was likely saturating the solution, and the digestion reaction stopped. Pouring the standards into 500 ml Erlenmeyer bottles and adding some water to dissolve the salt led to the continuation of the digestion process. The Erlenmeyer bottles were covered with laboratory film with a needle-hole to keep an ambient pressure in the bottles while still hindering the evaporation of volatile chlorides.

Minute amounts of metallic iron were still left in the standard solutions once the digestion reaction had slowed to a negligible level. To complete the digestion, 1.1 ml of pure sulphuric acid was added to both standard solutions.

The resulting solutions were analysed for chlorides using Hach IntelliCAL ISECl181 ion selective electrode using the double standard addition described in Chapter 5.4.5. Standard A was measured first undiluted, then diluted with RO water in ratios 1:2 and 1:4. The data agreed with the calculated values, indicating that no significant amounts of chloride had been lost. Most accurate measurements were achieved from 1:2 dilution, so standard B was measured diluted. Again, the results were in very good agreement with the calculated values.

Measurements with the Sherwood Scientific Model 926 were also attempted, but this method proved unsuitable. Subsequent measurements from the same solution showed wildly different results, and after a few measurements, the instrument ceased to give any measurement. This was unfortunate, as measurements using the chloridometer would have been much more convenient than the ion-selective electrode measurements.

However, it must be noted that the chloride concentration in these standards was significantly higher than that generally measured from the actual samples. Small losses in volatile chloride are unlikely to be detected, considering the accuracy of the ion-selective electrode. Also, the standards did not contain the impurities in the actual samples, so it is uncertain to what degree the results are representable. The low residual chloride concentrations coupled with the complex sample matrixes of the actual samples led to more challenging analyses than those taken from these standards.

5.4.Quantitative chemical analysis

5.4.1. Chloride determination

Successful desalination depends on one's ability to monitor the chloride extraction process. Without a reliable method of measuring whether chlorides are present in the desalination solution, decisions about the treatment become guesswork.

Because of the importance of chloride analysis methods in archaeological conservation, several reviews and method descriptions aimed at the conservation community have already been published (Greiff and Bach 2000: 331-33; MacLeod 1984; North 1987: 248-52; Pearson 1981: 125-26; Rinuy and Schweizer 1982; Schmidt-Ott and Oswald 2006b; Scott and Eggert 2009: 141; Selwyn 2001; Semczack 1977; Wang et al. 2008). The methods can be divided into qualitative and quantitative analysis methods.

Qualitative methods can be used to analyse whether chloride is present in the treatment solution. The good side of qualitative methods is their quickness and ease of use. The most typical qualitative chloride analysis method is the so-called silver nitrate drop test, where a small amount of dilute silver nitrate solution is added to a sample of the treatment solution (Organ 1955; Plenderleith and Werner 1971: 201-02). Silver nitrate reacts rapidly with any chloride ions present, precipitating white silver chloride in the sample:

Equation 5-14

$$AgNO_{3(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)} + NO^-_{3(aq)}$$

This cloudy precipitate needs to be visually observed in the sample, which means that the transparency and the colour of the sample greatly influence the detection limit of the method. Precipitation is most intense in samples with high chloride concentrations but becomes weaker the more dilute the solution is. Trials using artificial samples have shown that 5 mg/L chloride concentration is a likely realistic detection limit, even though lower concentrations may be detected under ideal conditions (Greiff and Bach 2000; Semczack 1977).

Quantitative methods not only measure whether chloride ions are present in the solution but also their concentration. A wide range of measurement methods have been used for this purpose, including various types of titration (e.g. Drews et al. 2013; Nestor G. González et al. 2004; Guilminot et al. 2012; Hamilton 1998; North 1987: 248-52; Rathgen 1905: 61-66; Selwyn 2001; Sörling 1924: 41-42), ion chromatography (Drews et al. 2013; Gonzalez et al. 2007; González-Pereyra et al. 2013; Schmidt-Ott and Oswald 2006b), ion-selective electrodes (Al-Zahrani 1999; Beaudoin et al. 1995; Carlin et al. 2001; Loeper-Attia and Weker 1995;

Plenderleith and Werner 1971: 201-02; Rimmer 2010; Selwyn and Logan 1993; Semczack 1977; Wang et al. 2008; Weker 1989), Quantab quick test strips by Hach Lange (Carlin et al. 2001; Drews et al. 2013; Gonzalez et al. 2007; Sullivan et al. 2013; Ternisien et al. 2013), quick test kits by Merck Millipore (Norlander and Mattsson 1996; Schmidt-Ott and Oswald 2006b; Wang et al. 2008), and photometric analysis (Kuhn et al. 2011; Schmutzler and Eggert 2010a; Schmutzler 2012; Wunderlich 2000). Flow-through cell based on ion-selective electrodes have also been used (Loeper-Attia and Weker 1995; Weker 1989).

As the vast array of analysis methods implies, chloride analysis is a challenge that can be approached in many ways. No chloride analysis standardisation has occurred in the conservation field, and laboratories often do not have the resources or competence to conduct extensive testing and quality control to verify the reliability of their method. To some extent, this applies to research as well as daily treatment.

Usually, chloride analysis equipment is intended for samples with near-neutral pH and low ionic strength. A typical desalination solution sample does not fulfil either requirement. The pH of alkaline desalination solutions falls between 12 and 14, and alkaline sulphite solutions contain sulphate ions in concentrations usually ranging between 0.05M and 0.5M. A wide array of ions can be leached out of the objects during treatment (Degrigny and Lacoudre 1999: 119; Norlander and Mattsson 1996: 42-47; Selwyn and Argyropoulos 2005: 90-92), which further complicates the composition of treatment solutions.

The compound detected, quantified, or studied is called the analyte in analytical chemistry. All else that the sample contains is called the sample matrix. In the case of chloride measurements from desalination solutions, chloride ions would be the analyte, and all other compounds – the treatment solution with substances other than chloride leached from the objects – form the sample matrix.

This means that much in the same way as each archaeological object is the unique result of a complex interaction between the object and its burial environment, the composition of the desalination solution results from a unique interaction between the object and the solution. Its composition is unknown.

The matrix usually interferes with analysis methods, so it is essential to calibrate the analysis method with standards mixed in solutions that mimics the sample matrix as closely as possible and see whether the method is compatible with the samples in the first place.

Desalination solution samples can be considered to have complex, unknown matrixes and detecting chlorides in parts per million range from such mixtures is a challenging task. It is impossible to know accurately how an unknown matrix will affect an analysis. In the case of desalination solutions, the best that can be done is usually mixing the standard solutions in a matrix similar to the fresh treatment solution. However, this does not take into account the other substances that could have leached out of the objects besides chlorides and could interfere with the analysis.

It is perhaps unsurprising that some sources exhibit a scepticism towards chloride analyses carried out in conservation laboratories, considering the challenges (Greiff and Bach 2000: 332-33; North 1987: 252). At the very least is good practice to carry out basic quality control to maintain a realistic idea about the accuracy of one’s measurements.

Residual chloride analysis is another field where quantitative methods are necessary. There are several ways of carrying out residual chloride analysis, the most traditional of which is digesting the test subjects in acid and measuring the chloride concentration of the resulting solution (Al-Zahrani 1999; Drews et al. 2004; Rimmer 2010; Rinuy 1979; Rinuy and Schweizer 1982; Schmutzler 2012; Watkinson 1996; Watkinson and Al-Zahrani 2008).

These measurements can be more demanding than measuring chloride concentrations from treatment solutions. Acids digest various corrosion products, siliceous and organic compounds, and metallic iron far more efficiently than alkaline desalination solutions, leading to a more complex sample matrix. Also, residual chloride levels are typically low, which amplifies the effect of even relatively minor errors.

Considering that the composition of the corrosion crust is usually unknown for any individual object, there is a significant potential for interfering ions. The concentration of other ions in the solution is disproportionately higher than the chloride concentration. How much of a problem this is depends on the type of ions in the sample, but since this cannot usually be determined, we cannot know what effect they will have on the measurements.

Only some studies address problems with residual chloride measurements from acid-digested samples considering the total number of studies with residual chloride analyses. Rinuy (1979: 139) discovered that acid-digested residual chloride samples could not be analysed by potentiometric titration. However, this method has been successfully employed using a chloride specific instead of a silver-specific electrode to determine the titration endpoint (Drews et al. 2004; Nestor G. González et al. 2004). The reported detection limit of “less than 100ppm” was relatively high.

Schmutzler and Eggert (2010a) have raised concerns about losing volatile chloride during acid digestion. The effect was most significant when samples were digested in hot nitric acid in uncovered containers, as had been standard practice in previous studies. The authors also noted the lack of detailed method descriptions in previous studies. This, and the need for standardised residual chloride analysis methodology (Schmutzler and Eggert 2010b), makes it difficult to compare results.

One of the most significant issues with wet chemical residual chloride analysis is that it requires the destruction of test objects. This has led many authors to seek various non-destructive alternatives, such as instrumental neutron activation analysis or prompt gamma activation analysis (INAA and PGAA, respectively) (Schmutzler et al. 2019; Selwyn and Argyropoulos 2006; Watkinson et al. 2014). Also, Schmidt-Ott et al. (2017) used a combination of neutron and computed tomography to map the location and quantity of chlorides before and after treatment. While the results of these studies are promising, the complex analysis equipment used in them requires collaboration with laboratories with such facilities.

Chloride concentrations were analysed for two different purposes in this study. Firstly, the chloride concentration of each treatment batch was measured weekly to understand the extraction rate in each batch. Secondly, residual chloride was measured from all nails that finished their treatments, as well as the total chloride concentration of two untreated batches of nails.

A different methodology was required to carry out these measurements. Extracted chlorides could be analysed from samples of the treatment solutions. This was carried out with a coulometric titrator Model 926 by Sherwood Scientific.

To measure total and residual chlorides, the nails analysed had first to be digested in acid. Chloride concentrations were measured from the resulting solution. The chloridometer used in the analysis of extracted chlorides could not be used with these samples, so ion-selective electrodes were used instead. The electrode first used, combination electrode ISECL181 by Hach would wear out during the series of measurements and had to be replaced.

Due to supply shortages by the Covid pandemic, a replacement ISECL181 electrode could not be acquired in time, so a different set of electrodes, an ELIT 8261 chloride selective electrode with an ELIT 003n double junction liquid acetate reference electrode, was used towards the end of the measurement series.

The qualitative and quantitative analysis methods used in this study are very different, and it is best to take a closer look at them separately.

5.4.2. *Coulometric titration*

Titration is a well-established method in analytical chemistry and has a long history in archaeological conservation. Titration is an analysis method where a reagent solution – the titrant – is added to the analyte until the reaction between the two is complete. Since the concentration of the titrant is known, the concentration of the analyte can be calculated from the amount of titrant used. For the method to work, the reaction between the titrant and the analyte must be fast, and the reaction must have a large equilibrium constant. In other words, the added titrant needs to react entirely and quickly with the analyte.

The point at which all analyte has reacted with the titrant is called the equivalence point of the titration. The accuracy of the analysis depends greatly on accurately detecting this equivalence point. However, detecting the equivalence point usually depends on detecting unreacted titrant in the sample. At this point, the equivalence point has been slightly exceeded, and therefore it is called the end point of titration rather than the equivalence point. An accurate titration depends on having the end and equivalence points as close as possible. Various actions can be taken to increase accuracy, but as with any measurement, removing uncertainty is impossible.

Coulometric titrators, also known as chloridometers, have been mentioned in a conservation context in Australian sources from the late 1970s to the late 1980s (MacLeod 1984, 1987; North and Pearson 1978c: 29; North 1987: 251). The method is fundamentally argentometric titration, where silver ions are created by anodically dissolving silver wire. The device detects the endpoint by measuring the current between two auxiliary silver electrodes, which will increase once all chloride has been precipitated as silver chloride and free silver ions start to be released into the solution. Therefore, the method is also known as amperometric titration.

Anodic dissolution of metallic silver is generally a far more accurate method of introducing silver ions into the sample than the volumetric addition of titrant containing silver ions. This enables the use of tiny sample volumes with the coulometric titrator. In the case of Sherwood Scientific Model 926, only 500µL of sample is required per measurement.

Coulometric titrators are semi-automatic and come with the pros and cons of automatic equipment. On the one hand, “push-button” functionality saves time, but on the other hand, it can also result in a misleading sense of accuracy. Sherwood Scientific gives an accuracy of 2 mg/L and linearity of 3 mg/L for their device (Anonymous 2011), but that does not mean that this accuracy can necessarily be achieved from complex samples in a laboratory with limited chemical competence. It is always up to the operator to understand what method lies behind the results of an analysis and what possible sources of error might be present.

To test the suitability of Model 926 with desalination solution samples, a test series was conducted with chloride standard solutions mixed in matrixes imitating NaOH and AS wash solutions. The results from these tests were very promising. At least the reagents do not appear to cause a significant error in the results, but it should be noted that the tests represent a best-case scenario regarding the complexity of the sample matrix. The device was also tested with standard solutions imitating residual chloride samples. Here coulometric titration was not the way forwards, so a different analysis method was necessary.

5.4.3. Ion-selective electrodes

The definition of an electrode covers a wide array of instruments. Karl Camman, in his publication “Working with Ion-Selective Electrodes” (1979: 6), defines electrodes as “[D]evices with which one can detect the movement and separation of charges occurring at phase boundaries, as well as induce and vary such processes utilising forced current flow”. In other words, an electrode is the part of an electric circuit where current is passed between a solid and a non-solid phase, whether liquid, gaseous or even plasma. Electrodes to measure voltages that provide chemical information is called potentiometry.

Even though the range of electrodes is broad, we are mainly interested in ion-selective electrodes – ISEs – in chloride analytics. These are typically analytical devices about the size of a pencil that measure the analyte's activity by immersing the electrode's detector end into the sample. At the detector end, the ISE has a sensing element called a membrane, the potential of which is dependent on the activity of the analyte in the sample.

The most typical ISE is the pH electrode, which many conservators are familiar with, even if they have had nothing to do with chloride analytics. In a similar way that the glass membrane of the pH electrode is sensitive to the concentration of hydrogen ions, the membranes of other ISEs are sensitive to their specific ions.

Glass pH electrodes are the oldest of ISEs, and their history dates to the beginning of the 20th century. It took longer for electrodes for other ions to become available, but significant development occurred in the 1960s. (Mikhelson 2013: 7-9) Chloride selective electrodes were becoming available when Plenderleith and Werner wrote their classic on the conservation of antiquities and works of art (1971: 201-02).

Ion-selective electrodes have become common thanks to their relatively low cost, functionality, and ease of use. Many modern titration methods also depend on potentiometric analysis, which testifies to their usefulness. However, there are limitations to these methods that can go unnoticed in conservation work.

When two different conductive phases come into contact, an electric potential will rise at the phase boundary. Ion-selective electrodes utilise this phenomenon. The typical structure of an ion-selective electrode is an ion-selective membrane encased in a cylindrical casing. When the membrane end of the electrode is immersed in the sample, an electric potential difference will rise across the membrane-sample interface.

The membrane is built to bind the analyte ion on its surface selectively. The higher the activity of the analyte in solution, the more these ions will be bound at the membrane. This accumulation of ions will change the voltage at the interface between the sample and the membrane. Thus, the electrode works as a sensor where the input signal is the activity of the analyte ion, and the output signal is the voltage across the membrane-sample interface.

It is not possible to measure this potential directly. An electric potential can only be measured as a potential difference in relation to another potential. Using ion-selective electrodes, this is achieved using a so-called reference electrode. The role of the reference electrode is to provide a stable potential that the working electrode's potential can be compared against. The reference electrode can be built into the same electrode body, in which case we are talking about a combination electrode, or it can be constructed separately into its own body. Nevertheless, a reference must be present for the measurement to be possible. The instrument's signal is the potential difference between the ion-selective and the reference electrodes. For the sake of simplicity, this value is referred to simply as electrode potential in the following text.

The output signal of an ideal ion selective electrode would depend on the activity of the analyte ion according to the Nernst equation (Rundle 2000):

Equation 5-15

$$E = E^0 + (2.303RT/nF) \times \log(A)$$

Where E = the total potential (in mV) developed between the sensing and the reference electrodes

E^0 = is a constant which is characteristic of the particular ISE/reference pair

2.303 = the conversion factor from natural to base10 logarithm

R = the Gas Constant (8.314 joules/degree/mole).

T = the Absolute Temperature

n = the charge of the ion

F = the Faraday Constant (approximately 96 500 coulombs)

Log(A) = the logarithm of the activity of the measured ion.

From the Nernst equation, we can see that as long as the temperature stays constant, the potential between the working and the reference electrodes depends on the logarithm of the activity of the measured ion. If the electrode's potential is plotted against the logarithm of the analyte, the 2.303RT/nF is the slope of the resulting line.

Real-life electrodes practically never behave exactly like the theory suggests. This is why testing the electrode's behaviour and generating the slope experimentally using standard solutions with known analyte concentrations is necessary. Electrodes also wear out over time, which usually leads to a lowering of the slope. This decreases the accuracy of the electrode, as a lower slope makes it more difficult to detect changes in the analyte's activity.

No membrane binds only the analyte ion but shows affinity to other types of ions, which is another source of inaccuracy in ISE measurements in addition to changes in the electrode slope. The membrane is created so that it has a high affinity for the analyte ion while having as low affinity as possible for other ions. However, some affinity for interfering ions will always remain. This stresses the importance of knowing the composition of the sample matrix.

Since ISE measures the activity of the analyte in solution, the measurement depends on the ionic strength of the solution. The activity of the same concentration of ions will be different in sample matrixes with different concentrations due to interference. In dilute solutions, the ionic activity is roughly equal to the concentration of the ion, but these values start to deviate as ionic strength increases.

One can visualise this effect by imagining the microscopic reality next to the ion-selective membrane. In high ionic strength solutions, the interface between the solution and the membrane gets crowded, and the membrane can "sense" fewer analyte ions due to this interference. If this phenomenon is not accounted for, it leads to an erroneously low estimate of the concentration of the analyte ion. This problem is usually overcome by adding what is known as a Total Ionic Strength Adjuster (TISAB) to the samples. The role of the TISAB is to standardise the ionic strength of the standard and sample solutions to such a high level that the differences can be ignored.

The ISE producers usually provide a TISAB solution developed specifically for their electrodes. These typically contain ions that will affect the total ionic strength of the solution while not interfering with the analysis, but they can also have other substances that are supposed to suppress the effect of interfering ions. It must be noted that TISAB will only impact relatively dilute samples. Samples with high ionic strength will not benefit from TISAB since if the ionic strength of the samples are already close to that of the TISAB, then adding TISAB will understandably not be an effective way of levelling the differences in their ionic strength.

In such a case, dilution by TISAB is a more effective way. In this case, a small amount of sample is added into a larger volume of TISAB solution.

There are several types of ion-selective membranes. Chloride selective electrodes have a pellet that has silver chloride as its main constituent, which makes it sensitive to iodide, cyanide, sulphide and silver ions. In the presence of sulphide ions the pellet can be irreversibly damaged. For conservators working with AS solutions it is important to notice that also sulphite ion interferes with the pellet (Loeper-Attia and Weker 1995: 163; Weker 1989)

5.4.4. Residual chloride measurements using ISEs.

Residual chloride samples were demanding to measure. Digestion in acid led to samples with unknown, complex matrixes with high ionic strengths and low chloride concentrations.

At the end of the digestion, the solutions were close to the saturation point of iron(II)sulphate, which at room temperature is roughly 0.1 M/L. This is the value in pure solutions, so in the case of samples, it can be assumed that the solubility is lower due to the interference by other soluble ions. After digestion, the pH of the solutions had to be adjusted, which could mean an addition of over 20 grams of sodium hydroxide. If we assume that the sodium hydroxide reacted with excess sulphuric acid according to the reaction:

Equation 5-16

$$2NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$$

When the average sample volume at this stage was in the range of 275 ml, the resulting concentration of sodium sulphate alone would be close to 1 mol/L: a high ion concentration for an ISA measurement. Considering that the samples likely contained a lot of other ions in unknown concentrations while the analyte concentration was low, it was impossible to standardise the activity using ISAB. This ruled out direct potentiometry.

Because of the demanding nature of the samples, it was decided to use a gravimetric double standard addition. In this method, the electrode is immersed in a known sample volume and the stable potential is read. Then, a standard solution containing a known analyte concentration is added until the electrode potential changes by some 20-30 mV. The solution is thoroughly mixed, and a new stable potential is recorded, after which a second standard addition is carried out like the first one. (Camman 1979: 143-44; Rundle 2006)

A concentrated standard should be used not to change the ionic strength of the solution too much. However, simultaneously the standard should be dilute enough to allow for an accurate measurement of the volume of the addition. For this purpose, the standard was added using a dropping bottle that was measured before and after the addition. This was done because of the greater accuracy of gravimetry in comparison to volumetry.

The benefit of this method is that the two standard additions practically calibrate the electrode in the same solution where the measurement is carried out. When the concentration of the standard is known, as well as the volumes of the two additions, the electrode slope specific to the solution at hand could be calculated. Using this slope, the initial concentration could be interpolated.

However, the double standard addition method has limitations. Firstly, the starting concentration and the subsequent concentrations after the standard additions must lie on the linear region of the electrode. If this precondition is violated, the interpolation will give erroneous results. Another precondition is that the sample must be free of interfering ions.

A Microsoft Excel sheet provided by Nico2000 was used to carry out the calculations (Rundle and Cui 2013). Each sample was measured at least three times whenever the solution volume allowed more in case the results were spread or if subsequent measurements tended towards higher or lower values. Mean concentration and standard error were calculated using the measurement data.

Despite this laborious process, several sources of uncertainty remain in the residual chloride measurements. Stabilisation times varied a lot from solution to solution. Generally, these were long and unstable readings were not uncommon. Stabilisation times exceeding 15 minutes after each standard addition were common. With such long stabilisation times, it wasn’t easy to distinguish whether the electrode potential was stabilising or drifting.

There was no way to check the samples for interfering ions, so their effect on the results is unknown. The ions interfering with a chloride ISE are iodide, bromide, cyanide, sulphide, and silver ions. Sulphide and iodide, if present in larger than trace amounts, can damage the pellet.

Two different ISE units were used to measure residual chloride. The first one, ISECl181 by Hach, was a gel-filled combination electrode. The internal Ag/AgCl reference was a double-junction reference with porous-pin and annular porous PTFE junctions. The external reference was filled with a Dritek Gel, the composition of which is not known.

The electrode was worn out during the series of measurements, indicated by increasingly long stabilisation times and drifting measurements. The reason for this is unknown, but such problems are usually caused by the reference electrode becoming contaminated. The closed, maintenance-free structure of the electrode meant that the fill solution could not be renewed, and the junction could not be cleaned. The outer junction turned increasingly rusty brown during the measurements, indicating probable contamination by iron oxides.

The electrode was worn out during the Covid-19 crisis, and the delivery time for a replacement was prohibitively long. Thus, it was decided to change the electrode type in the middle of the measurement series. A replacement was purchased from Nico2000, an ELIT 8261 crystal membrane chloride ISE and a separate double junction lithium acetate reference electrode, ELIT 003n. Measurements were carried out using an ELIT Computer Interface/Ion Analyser.

The manuals for these two electrodes give different selectivity coefficients for interfering ions. While Hach reports a coefficient of < 0.1 for all interfering ions, Nico2000 provides no exact coefficients stating that they are context-sensitive. Nico2000 warns that all the interfering ions could cause significant interference if present in higher than trace amounts.

To eliminate interfering ions, Nico2000 suggests mixing the samples with a sodium bromate buffer at a ratio of 1:1. The problem with this approach is the low chloride concentration of the solution: diluting the samples this much would make the chloride undetectable. This was also why sample addition – which otherwise would have been a good approach considering the high ionic strength of the samples – had to be ruled out.

The procedures for these two electrodes were principally the same but differed a little in practice. The procedures are composed using the producer's recommendations.

5.4.5. *Double standard addition using Hach ISECl181 chloride ISE*

A 25 ml sample was pipetted into a tall 50 ml glass beaker with a magnetic stirrer. The stirrer was rotated at a 150 r/min pace, and the electrode was immersed at least one inch (25.4 mm), ensuring no air bubbles were left adhering to the crystal.

The measurement was carried out using the "Continuous measurement" mode built into the Hach Hq440D laboratory meter to keep the measurement value from freezing. This was done since it was found that the measurements achieved using the "Push to measure" mode were unreliable, as brief periods of stability between unstable values were common. The built-in stability criterion of 0.1 mV/min was used only as a reference when judging whether the value had indeed stabilised or not. The final judgment was done subjectively.

The manual for the electrode set the lower end of the linear region at 10 mg/L. However, this is likely true only under ideal conditions: fresh electrodes and pure solutions. Whenever the initial millivoltage suggested a chloride concentration below 10 mg/L, the sample was spiked with 250 µL of 1000 mg/L chloride standard, which would theoretically increase the concentration by roughly 10 mg/L (9.90099 mg/L). This would later be subtracted from the final reading. Spiking was carried out using an adjustable 1000 µL micropipette (Finnpipette F1).

Measurements were recorded by hand and in millivolts. Depending on the estimated starting concentration, 1000, 5000 or 10 000 mg/L standard solution in a dropping bottle was chosen for the standard additions. The most used standard was the 1000 mg/L standard, as the chloride concentrations were generally low. The bottle was weighted, after which the standard was added dropwise until the potential had changed by > 20 mV, at which point the weight of the bottle was recorded, and the reading was allowed to stabilise. Once the reading was deemed stable, it was recorded, and a second addition was carried out similarly to the first one.

5.4.6. *Double standard addition using ELIT 8261 chloride ISE and an ELIT 003n reference electrode.*

A 50 ml sample was pipetted into a 100 ml PP beaker, and the electrodes were immersed. Electrode stability had to be determined subjectively as no built-in stability criterion existed. The initial chloride concentration was estimated from the initial reading. The manual for the electrode set the lower end of the linear region at 7 mg/L. However, this is likely true only under ideal conditions: fresh electrodes and pure solutions. Whenever the initial millivoltage suggested a chloride concentration below 10 mg/L, the sample was spiked with 500 µL of 1000 mg/L chloride standard, which would theoretically increase the concentration by roughly 10 mg/L (9.90099 mg/L). This would later be subtracted from the final reading. Spiking was carried out using an adjustable 1000 µL micropipette (Finnpipette F1).

According to the manual, the most stable readings would be achieved in an unstirred solution, so no mixing was done during stabilisation. Once the initial millivoltage had stabilised, the value was recorded, and 1000, 5000 or 10000 mg/L chloride standard solution was chosen for standard addition depending on the initial concentration of the sample. The 1000 mg/L solution was used the most as chloride concentrations were typically low.

Standard was added from a dropping bottle weighted before the addition. The solution was thoroughly mixed during the addition by swirling the beaker by hand. Once the potential had increased by 20-30 mV, the dropping bottle containing the standard solution was weighted again, and the potential was left to stabilise. Once stable, the reading was recorded, and a second addition was carried out like the first one.

One could see a rusty brown precipitate building up in the porous pin junction of the lithium acetate reference electrode. This was regularly cleaned by soaking the electrode in a 10 % HCl solution, followed by a thorough soaking in RO water and 0.1 M lithium acetate to renew the electrode.

5.4.7. LDO measurements

The oxygen content of the treatment solutions was determined weekly using a Luminescent Dissolved Oxygen (LDO) probe. The method uses a luminescent material excited by a blue light emitted by the sensor. Once excited, the luminescent material relaxes, emitting red light, measured by the sensor. An internal red light is used for calibration. The luminescence happens after a delay, the length of which depends on the oxygen concentration of the solution. Thus, the oxygen concentration can be calculated from the time between the flashes of blue and red light. (Bier 2018: 39-40)

Dissolved oxygen should be measured from samples not exposed to the atmosphere. As soon as the sample is exposed to the atmosphere, atmospheric oxygen will start to dissolve in it, causing a positive error. Unfortunately, isolating the samples from atmospheric oxygen was impossible in this study as the containers had to be opened for measurement. It was attempted to keep the error due to atmospheric oxygen as low as possible by measuring dissolved oxygen quickly after opening the container.

DO levels were determined with a luminescence dissolved oxygen probe (Hach Lange LDO101 probe). The performance of the LDO probe was tested with a solution of 0.1 M ascorbic acid in 0.23 M sodium hydroxide. It took about half an hour before the probe finally stabilised at 0.07 mg/L oxygen.

Such a long stabilisation time was impractical considering the number of test solutions, so it was decided to use the probe with the highest stability criteria (0.05 [mg/L]/min) built into the laboratory meter (Hach Lange HQ440D). Using this criterion in the same deoxygenated standard solution measured 0.18 mg/L oxygen in about two minutes.

The reading was usually slowly drifting towards a lower value when the stability criterion was met. This drift was ignored, which means that DO concentrations are likely overestimated. However, achieved precision in combination with a large number of readings allows a meaningful comparison of treatment solutions.

5.4.8. pH measurements

pH of the solutions was measured using a gel-filled combination electrode by Hach Lange (pHC101). The electrode was calibrated before the series of measurements for the day was begun. A pH electrode is fundamentally an ion-selective electrode with an H^+ ion-sensitive membrane, usually composed of a thin layer of glass. The glass membrane is one of the most common and accurate types of ion-selective membranes. However, pH electrodes have their limits.

A typical pH electrode struggles to measure pH accurately in solutions with low ionic strengths, as there needs to be more ions present to achieve a stable potential across the membrane. Also, high pH values present another difficulty for two reasons. Firstly, there are no stable calibration solutions above pH 10. Calibration solutions with a very high pH should be freshly mixed before calibration, and any error in preparation will naturally be reflected in the results. This means that using pre-mixed calibration solutions, the measurements will not be within the calibrated area.

Usually, this is not much of a problem since pH electrodes are known for their linearity and stability. However, the electrode signal ceases to be linear on high pH levels, and the Nernst equation no longer applies. This leads to a systematic error in the measurements.

These problems can be avoided using specialised equipment and methodology, such as custom-made calibration solutions and electrodes explicitly designed for high pH values. Neither solution was used in this study, so the pH measurements should be cautiously approached.

5.4.9. Conductivity measurements

Conductivity is the ability of a material to pass electric current. The conductivity of aqueous solutions depends on the concentration, valence and mobility of ions and temperature. Conductivity measurements were conducted using a Hach Intellical CDC401 4-poles graphite conductivity cell.

Conductivity was measured weekly in connection with the chloride measurements. The conductivity of ROw and alkaline solutions differed by several orders of magnitude making measurements challenging. Also, Row solutions were heavily contaminated with corrosion products that stuck to the probe’s surface and made measurements difficult. A stable reading could not always be achieved.

The probe was regularly cleaned with 10 % HCl according to the producer’s instructions. However, errors due to corrosion products contaminating the probe could not be entirely avoided, as this would have necessitated cleaning in acid after each measurement. This would have been prohibitively laborious and risked contaminating the solutions with chloride. However, the achieved accuracy was enough to spot general trends in the conductivity of the solutions and compare the different treatments.

6. Results

6.1.Descriptive statistics of the residual chloride data

Large deviations and a positive skew characterised the residual chloride data. The average residual chloride was about 190 ppm with a standard deviation of 160 ppm. This leads to a relative standard deviation of over 80 %. It is not easy to reach statistical significance with this spread data, even with relatively large differences in means. Very large sample sizes would be necessary, which is difficult to achieve with the resources available in the cultural heritage field.

Apparent differences in means emerged between the test factors. The mean residual chloride achieved in alkaline sulphite was about 220 ppm, while NaOH resulted in an average residual chloride content of roughly 160 ppm. Nails treated in ambient pressure had a residual chloride concentration of 210 ppm, while those treated in a vacuum would have a lower concentration of 170 ppm. Finally, the most significant difference was observed between non-pre-cleaned and pre-cleaned samples, which had average chloride concentrations of 220 ppm and 140 ppm, respectively.

The raw data were tested for normality since it is one of the preconditions for most statistical analyses, including the ANOVA test. All categories failed both Shapiro-Wilk and Kolmgorov-Smirnov tests of normality, which is unsurprising considering the skewness of the data. Thus, the data violates one of the preconditions of the ANOVA test.

Specimen number 246 was removed from the sample as an outlier. With a residual chloride concentration of 1600 mg/L, it stands out from the rest of the specimens. The nail lost over 85 % of its weight in cleaning, which also sets it apart.

6.2.Factorial analysis

Three-way ANOVA tests were carried out using SPSS (Version 29.0.0.0 [241]) with solution type, pressure and cleaning stage as fixed factors and residual chloride concentration as the dependent variable, measured as parts per million (ppm). Fixed factors were all binary. The two levels of solution type were NaOH and Alkaline sulphite, the levels for pressure were an ambient and partial vacuum, and the cleaning stage was divided into pre-cleaned and non-pre-cleaned.

Four different ANOVA tests were carried out.

1. ANOVA using cleaned weights for the pre-cleaned samples and untransformed data.
2. ANOVA using before-cleaning weights for the pre-cleaned samples and untransformed data.
3. ANOVA using cleaned weights for the pre-cleaned samples and log-transformed data.
4. ANOVA using before-cleaning weights for the pre-cleaned samples and log-transformed data.

Each of the three-way ANOVA tests had seven null hypotheses that were answered individually:

1. H_0: no significant difference in means of factor 1.
2. H_0: no significant difference in means of factor 2.
3. H_0: no significant difference in means of factor 3.
4. H_0: no interaction between factor 1 and factor 2.

5. H_0: no interaction between factor 1 and factor 3.
6. H_0: no interaction between factor 2 and factor 3.
7. H_0: no interaction between factors 1, 2 and 3.

The results of these four ANOVA tests are summarised below.

6.2.1. Results of the ANOVA test using cleaned weights for the pre-cleaned samples and untransformed data.

All data failed to pass the Shapiro-Wilk test of normality with a p-value of < 0.001 across all factors. The data is positively skewed and violates the normality prerequisite. Results must be approached with care.

The data passes Levene's test of equality of variances with a p-value of 0.123. The p-value is low but above the chosen α level of 0.05. The data fulfils the prerequisite of equal variances between the factors.

1. H_0: we fail to reject the null hypothesis that solution type has no significant effect on residual chloride concentration:

   F = 1.941
   p = 0.167

2. H_0: we fail to reject the null hypothesis that pressure has no significant effect on residual chloride concentration:

   F = 1.791
   p = 0.184

3. H_0: we reject the null hypothesis that the cleaning stage has no significant effect on residual chloride concentration:

   F = 6.494
   p = 0.013

   There is enough evidence to accept the H_a that the cleaning stage has a significant effect on residual chloride concentrations.

4. H_0: we fail to reject the null hypothesis that there is no interaction between solution type and pressure:

   F = 0.149
   P = 0.701

5. H_0: we fail to reject the null hypothesis that there is no interaction between the solution type and the cleaning stage:

   F = 1.468
   p = 0.229

6. H_0: we fail to reject the null hypothesis that there is no interaction between the cleaning stage and pressure:

   F = 0.211
   P = 0.648

7. H_0: We fail to reject the null hypothesis that there is no interaction between solution type, pressure, and cleaning stage:

   F = 0.210
   p = 0.648

   α = 0.05

6.2.2. Results of the ANOVA using cleaned weights for the pre-cleaned samples and log transformed data.

The log-transformed data passes the Shapiro-Wilk test divided factor-wise, except for the non-pre-cleaned group, which fails the Shapiro-Wilk test with a p-value of 0.044. The result is at the edge of the 0.05 α level. The log-transformed data complies better with the normality of data prerequisite than the raw data but does not fulfil it completely. Visual examination of the Q-Q plot and histogram reveals that the log-transformed data under the non-pre-cleaned factor follow normality well except for some low-level outliers.

Levene's test of equality of variances reveals that the data fails to meet the prerequisite for equal variances across the factors with a p-level of 0.031. The log-transformed data violates the prerequisite of equal variances across factors. The results must be approached with caution.

1. H_0: we fail to reject the null hypothesis that solution type has no significant effect on residual chloride concentration:

   F = 2.223
   p = 0.140

2. H_0: we fail to reject the null hypothesis that pressure has no significant effect on residual chloride concentration:

   F = 1.697
   p = 0.196

3. H_0: we reject the null hypothesis that the cleaning stage has no significant effect on residual chloride concentration:

   F = 4.425
   p = 0.038

   There is enough evidence to accept the H_a that the cleaning stage has a significant effect on residual chloride concentrations.

4. H_0: we fail to reject the null hypothesis that there is no interaction between solution type and pressure:

   F = 0.594
   P = 0.443

5. H_0: we fail to reject the null hypothesis that there is no interaction between the solution type and the cleaning stage:

   F = 2.251
   p = 0.137

6. H_0: we fail to reject the null hypothesis that there is no interaction between the cleaning stage and pressure:

   F = 0.037
   P = 0.847

7. H_0: We fail to reject the null hypothesis that there is no interaction between solution type, pressure, and cleaning stage:

   F = 1.984
   p = 0.163

   $\alpha = 0.05$

6.2.3. Results of the ANOVA using before-cleaning weights for the pre-cleaned samples and untransformed data

All data failed the Shapiro-Wilk test of normality with a p-value of < 0.001 across all factors. The data is positively skewed and violates the normality prerequisite.

The data failed Levene's test of equality of error variances with a p-value of 0.001. The data violates the prerequisite for equal variances across the factors. The data fails two of the prerequisites of an ANOVA test, and the results must be approached with care.

1. H_0: we fail to reject the null hypothesis that solution type has no significant effect on residual chloride concentration:

   F = 1.808
   p = 0.182

2. H_0: we fail to reject the null hypothesis that pressure has no significant effect on residual chloride concentration:

   F = 1.209
   p = 0.275

3. H_0: we reject the null hypothesis that the cleaning stage has no significant effect on residual chloride concentration:

F = 25.176
p = <0.001

There is enough evidence to accept the H_a that the cleaning stage has a significant effect on residual chloride concentrations.

4. H_0: we fail to reject the null hypothesis that there is no interaction between solution type and pressure:

   F = 0.137
   P = 0.712

5. H_0: we fail to reject the null hypothesis that there is no interaction between the solution type and the cleaning stage:

   F = 2.157
   p = 0.146

6. H_0: we fail to reject the null hypothesis that there is no interaction between the cleaning stage and pressure:

   F = 0.023
   P = 0.881

7. H_0: We fail to reject the null hypothesis that there is no interaction between solution type, pressure, and cleaning stage:

   F = 0.293
   p = 0.590

   α = 0.005

6.2.4. Results of the ANOVA using before-cleaning weights for the pre-cleaned samples and log transformed data.

The log-transformed data passes the Shapiro-Wilk test divided factor-wise, except for the non-pre-cleaned group, which fails the Shapiro-Wilk test with a p-value of 0.044. The situation is similar to ANOVA using cleaned weights and log-transformed data since the uncleaned data is the same in these two groups. The result is at the edge of the 0.05 α level. The log-transformed data complies better with the normality of data prerequisite than the raw data but does not fulfil it completely. Visual examination of the Q-Q plot and histogram reveals that the log-transformed data under the non-pre-cleaned factor follow normality well except for some low-level outliers.

Levene's test of equality of variances reveals that the data fails to meet the prerequisite for equal variances across the factors with a p-level of 0.015. The log-transformed data violates the prerequisite of equal variances across factors. The results must be approached with caution.

1. H_0: we fail to reject the null hypothesis that solution type has no significant effect on residual chloride concentration:

   F = 0.773
   p = 0.382

2. H_0: we fail to reject the null hypothesis that pressure has no significant effect on residual chloride concentration:

   F = 2.999
   p = 0.087

3. H_0: we reject the null hypothesis that the cleaning stage has no significant effect on residual chloride concentration:

   F = 39.991
   p = <0.001

   There is enough evidence to accept the H_a that the cleaning stage has a significant effect on residual chloride concentrations.

4. H_0: we fail to reject the null hypothesis that there is no interaction between solution type and pressure:

   F = 0.892
   P = 0.347

5. H_0: we reject the null hypothesis that there is no interaction between the solution type and the cleaning stage:

   F = 4.586
   p = 0.035

   There is enough evidence to accept H_a that solution type and cleaning stage have a significant interaction.

6. H_0: we fail to reject the null hypothesis that there is no interaction between the cleaning stage and pressure:

   F = 0.373
   P = 0.543

7. H_0: We fail to reject the null hypothesis that there is no interaction between solution type, pressure, and cleaning stage:

   F = 1.578
   p = 0.213

   $\alpha = 0.05$

6.2.5. Summary of the ANOVA results

No dataset complied fully with the prerequisites of the ANOVA test, and all results should be approached cautiously. Log transformation of the data increased its compliance with normality but also caused variances to be more heterogeneously distributed across the factors.

The only consistent result is the significant effect of pre-cleaning the objects before treatment. Using weights after cleaning, the effect is significant at an α level of 0.05 but not at 0.01. If before cleaning weights are used, the result becomes highly significant, easily fulfilling the more stringent 0.01 α level.

The interaction between solution type and cleaning stage reached significance in the ANOVA test using log-transformed data and weights before cleaning for the pre-cleaned specimens. The p-level of 0.035 is only slightly below the 0.05 α level. Considering that the difference was observed only on one of the four ANOVA versions, this result is unlikely to be significant.

There are other results that failed to meet statistical significance but are nevertheless interesting. That a result fails to meet statistical significance does not invalidate it: it only means that a significant (greater than the chosen α level, usually 0.05) risk of an erroneous conclusion remains with the available data. The significance of the results depends on the size of the differences in means, the spread of the data, and the sample size.

Residual chloride data is usually heavily spread, and treatment and analysis are laborious. This limits the sample sizes that can be included in desalination tests, and failing to reach statistical significance is typical. Using a larger sample size could push the results below the chosen α level, but conservation institutions do not necessarily have the resources to do much replication. The sample size is always a compromise between reliability and costs.

Looking at the results that failed to meet significance, some trends emerge from the data: NaOH solutions outperform alkaline sulphite, and solutions under partial pressure outperform those under ambient pressure. The average p-value for both factors is around 0.2, which means there is a 1/5 chance that the observed differences in means are due to random variation. Without replication, it is impossible to know whether the difference is real or accidental.

The difference in favour of partial pressure fits desalination theory. The treatment solution could penetrate the corrosion layers more thoroughly with the help of a partial vacuum, and deoxygenation should aid in the extraction of chlorides through passivation – this should be an advantage in NaOH solutions, at least, which lack a chemical oxygen scavenger.

The difference between NaOH and alkaline sulphite solutions is harder to explain. Physically deoxygenated NaOH solutions have outperformed alkaline sulphite solutions in previous studies, but now it appears that alkaline sulphite does not outperform NaOH even in ambient pressure. Also, both solutions perform better in a partial vacuum, but NaOH solutions benefit more.

Random variations in the data could explain these differences. However, the analysis did not reveal any apparent benefits of using alkaline sulphite as a treatment solution. Considering the difficulties that adding sulphite into the solution entails, it would be a relief to omit it from the treatments.

The lowest residual chloride levels were achieved using NaOH solution in a vacuum. The residual chloride levels achieved in a vacuum with NaOH were roughly 40 % lower than in ambient pressure. The difference in means is quite large but fails to meet statistical significance due to the large standard deviations and limited sample sizes.

6.3. Treatment duration

The duration of the treatments appears to depend on the type of solution. The data was very limited, but a three-way ANOVA test was carried out using solution type, pressure, and cleaning stage as fixed factors and treatment duration as the linear dependent factor. The analysis confirmed that solution type had a statistically significant impact on treatment times, with an F value of 205.654 and a p-value < 0.001.

Tukey Honest Significant Difference (Tukey HSD) posthoc test reveals that the treatment times of all solution types differ from each other to a significant level. The pressure was another factor at the edge of a 0.05 α level, with an F value of 7.394 and a p-value of 0.053. Treatments in a vacuum took an average of 289 days, compared to treatments in ambient pressure, which took 250 days on average.

The shortest treatment times were reached using alkaline sulphite, with an average treatment time of 157 days with a standard deviation of 13 days, followed by NaOH with an average of 233 days and a standard deviation of 54 days. The progression of AS and NaOH treatments are compiled in Appendix 2. All alkaline sulphite treatments were finished within a relatively uniform timespan, while there was more deviation in the durations of sodium hydroxide treatments. Finally, reverse-osmosis water had an average treatment time of 494 days, but it must be noted that none of the water treatments was finished within the allocated time. How much time the water treatments would have needed to finish is unknown. The progress of ROw treatments is compiled in Appendix 2.

Chloride extraction was plotted against the square root of time to see whether it was diffusion based. The first bath extracted a significant amount of chloride. The chosen one-week measurement interval was too long to calculate the extraction rate for the first baths, as extraction had already slowed down by the second measurement. The efficient extraction period of the first bath was brief. A rapid extraction of soluble chlorides likely explains this.

Subsequent baths were linear against the square root of time in all batches, except batch 8, which appeared to follow the abrupt diffusion model outlined by Selwyn et al. (2001) with its slightly sigmoidal extraction curve.

6.4. Analysis of DO, pH, and conductivity measurements

An analysis of LDO measurements in this study have been published elsewhere (Pienimäki 2022). The lowest DO levels were achieved by combining physical and chemical deoxygenation. It should be re-evaluated whether 0.05 and 0.5 molar Na_2SO_3 perform similarly.

It is difficult to find previously published data on oxygen levels. C. G. Costain (2000) has published values that are comparable to those achieved in this study. However, the consistently low concentrations reached by Rimmer (2010: 81) could not be replicated. More data is needed on what DO levels are necessary to passivate iron.

pH was not found to drop in any of the solutions. This is probably because all treatments were carried out in closed containers. pH measurements were unreliable due to the high pH levels.

Conductivity showed opposite trends in ROw and alkaline solutions. As treatment progressed, the conductivity of ROw would increase as more ions would migrate into the solution.

However, in alkaline samples, conductivity would decrease as the treatment progressed. It is not known why this was happening.

6.5. Effects of the treatment on object condition

Changes in the condition of the treated objects were measured by carrying out the condition assessment before and after the treatment. Only physical integrity was assessed post-treatment. Both before and after condition data were based on assessments carried out by the author to minimise subjective error. However, this cannot be removed entirely, and condition assessment remains an ambiguous measure for damage.

A three-way ANOVA was carried out using solution type, pressure, and cleaning stage as fixed factors and change in physical integrity as the linear dependent factor. The data for changes in integrity is positively skewed, with the bulk of the data close to no change with a tail of negative values. It fails the Shapiro-Wilk test for normality with a p-value of < 0.001 and Levene's test for equality of variances with a p-value of 0.002. The data violates the normality of data and equality of variances preconditions for the ANOVA test, so the results must be approached with caution.

The cleaning stage was the only factor that had a statistically significant effect on changes in physical integrity, with an F value of 9.421 and a p-value of 0.003. Pre-cleaned objects suffered more changes to their integrity, with an average value of -1.18 on the CARS scale used and a standard deviation of 1.182. Non-pre-cleaned material had an average deterioration of -0.65 and a standard deviation of 0.914. The non-pre-cleaned material survived the treatment better.

However, it must be noted that pre-cleaned and non-pre-cleaned materials are not directly comparable since a condition assessment of all nails was carried out before cleaning. Damage due to cleaning is not reflected in the data. However, examining pictures taken after physical cleaning and treatment reveal that deterioration occurred during desalination.

Another thing to bear in mind is that since the condition assessment is based on visual examination, changes taking place within the corrosion layers cannot be assessed. This means that cracking and delamination hidden from sight by the bulky corrosion layers will not be reflected in the data. How deteriorated the non-pre-cleaned material would have been underneath the voluminous corrosion layers is unknown.

The effects of solution type and pressure did not reach statistical significance, though differences between these binary factors did emerge. The solution type came close to the chosen 0.05 α level with an F value of 2.790 and a corresponding p-value of 0.066. RO water and NaOH had the lowest effect on object integrity, while AS seemed to cause more deterioration. Interestingly, pre-cleaning seemed to make a particularly big difference in RO water regarding the deterioration of physical integrity due to treatment, with non-pre-cleaned objects surviving the treatment almost intact. In contrast, pre-cleaned objects suffered relatively significant deterioration. Differences due to pressure were minor but showed a trend of fewer changes in a partial vacuum. This would suggest that the expanding air within the corrosion layers does not cause significant damage to the object. On the contrary, a partial vacuum might even marginally protect the material from deterioration.

7. Future work

This study showed some interesting trends that should be investigated further. It is a pity that some observations could not be conclusively demonstrated, such as the effects of vacuum and solution type on the residual chloride levels achieved. This could be a question of sample size: eight specimens per treatment group is not much, considering the heterogeneity of archaeological iron.

None of the water-based treatments finished within the allocated time, so their residual chloride levels remain unknown. However, ROw was extracting significant amounts of chloride, even if this happened at an extremely slow pace compared to alkaline solutions. The extraction was so slow that using a fixed bath duration, there was a risk of determining that the treatment had finished.

This shows the benefits of monitoring the extraction against the square root of time: all the water-based treatments had good linearity when plotted this way, indicating when the extraction was still underway, just at a languid pace. Also, this linearity meant that extraction was getting increasingly slow when measured against the unaltered time units.

For example, the average extraction for batch 2 was so slow that it barely exceeded 5 milligrams per litre of treatment solution over a month. However, this indicated that the extraction process was still underway. Since this batch did not have time to finish, how much longer it could have taken is unknown. This begs the question, at what point should one determine that the extraction is negligible? Few conservation laboratories have the luxury of being able to treat their objects for years, especially considering that faster alkaline methods are available. It would still have been interesting to know what residual chloride levels could have been reached using ROw as the treatment solution had one had unlimited time available.

Drying the objects between treatments gave exciting results. In ROw solutions, drying resulted in an apparent increase in extraction rate for a short period. If we take Batch 5 as an example, almost a quarter of the total extraction occurred because of drying, and the process was not finished when treatment was terminated (see Appendix 2). More chloride could probably have been extracted had more time been available.

The author has observed a similar increase in extraction rate in practice using 0.1 M NaOH solutions, and Andersen (2006) has reported a similar phenomenon in desalinating iron pre-treated with plasma. The solution used in these studies was very dilute: 0.02 M NaOH.

Interestingly, no extraction rate increase seemed to occur using 0.5 M NaOH. Hydroxide ion concentration could play a significant role in this regard. Without further investigation, the reason for this can only be speculated. However, one could look for reasons that motivated Andersen to dry the objects in the first place: the theory that ferrous hydroxide could clog the pores within the corrosion crust.

Several authors have raised concerns about the possibility of ferrous ions turning into gel-like ferrous hydroxide that works as an efficient diffusion barrier inside the corrosion layer (Andersen 2006; Gilberg 1985; Greiff and Bach 2000: 324; Turgoose 1989; Watkinson and Al-Zahrani 2008: 79). The motivation behind drying is collapsing the iron hydroxide gel formed within the pores through drying and oxidation.

Usually, deoxygenating the treatment solutions is proposed as a solution to this problem, as removing oxygen from the solution stops the corrosion cycle and the creation of further ferrous ions. In addition, the lack of oxygen in the solution hinders further oxidation of any potential ferrous hydroxide into ferric hydroxide and oxyhydroxides.

However, an increase in extraction rate was observed in ROw solutions, while no such phenomenon was observed in alkaline solutions, whether oxygenated or not. This is surprising in the light of the theory. A possible explanation could be the wettability of the solution and its ability to extract chlorides from the anodic sites. Drying could increase porosity in the corrosion layers (Watkinson and Lewis 2004), increasing the accessibility of anodic sites for the treatment solution. However, it is impossible to explain the observations without a thorough analysis.

8. Discussion

It is dubious whether this study's conclusions will have a practical impact on the daily routines of conservation laboratories. The conclusions mostly open new questions that should be investigated before they can be applied confidently. Considering the unstandardised nature and poor repeatability of desalination research, carrying the research over with different materials and analysis equipment is probably not a motivating prospect.

Apart from the clear impact of cleaning the objects before treatment, the results of this study add to the long list of desalination studies with interesting yet inconclusive results. Desalination is a complicated and multifaceted process. Considering the resources generally available for conservation studies, conclusive results are perhaps much desired.

This makes evidence-based decision-making an arduous process of looking for trends in the mass of desalination studies. Conservation is by no means alone when confronting situations where decisions must be made in the face of uncertainty. On the contrary: it is the daily bread of sciences such as medicine and biology and any field dealing with complex real-life phenomena. Why conservation seems to have lost faith in science while the other fields facing similar complexity seem to have embraced it could have to do with how the conservation field approaches the scientific method.

Much time has passed since the enquiry by Schmutzler (2006). However, no significant changes have occurred in the conservation field, so should the enquiry be carried out today, the results would likely not have been significantly different. The feeling of being overwhelmed, which I believe many conservators are all too familiar with, still provides a perfect growing ground for professional cynicism.

When it comes to desalination, one is forced to accept that there are no methods available to guarantee the treated material's stability. Nevertheless, still, there are differences in the efficiency of the alternatives and our decisions matter. It should be remembered that the human brain, prone to black-and-white thinking, is terrible at intuitively understanding probability. We easily fall for biases and give too much emphasis to our personal observations. It is perhaps unsurprising that tradition and word-of-mouth strongly affect desalination methods in use today.

In the face of such uncertainty, every new study is like a piece of the puzzle that adds to our understanding of the complex phenomenon that desalination is. Looking at the overall picture to get the information for sound decision-making is necessary. This arduous process can easily get deprioritised in the face of everyday work, especially considering how little emphasis there appears to be on quality in our field. Quality is difficult to measure compared to quantity, so the number of objects treated and projects completed tends to dominate the yearly reports of conservation laboratories. We all believe we are doing a good job, and exposing oneself to outside criticism can be a very unpleasant idea. This is especially true since our field lacks generally agreed definitions of good practice, let alone institutions that would monitor its implementation.

It is generally agreed that making new information available should lead to better-reasoned conservation decisions. This is perhaps putting too much faith in the field. Experience has shown that there can easily be a gap of several decades between cutting-edge research and daily conservation practice. The way conservation education, research, and practice are structured all have roles in how the research front and daily treatment are separated. It is essential to remove these obstacles, as research in methodology has little value before it is applied.

8.1. Obstacles on the research front

There has been a schism between conservators and conservation scientists dating back to the 1980s. The conservators have voiced their disappointment with conservation science for being too elitist and detached from practice. Much effort seems to go into structural studies and descriptions of decay processes, with little regard for how these findings could be used in hands-on treatment. As such, conservation science risks being secluded in its ivory tower with little impact on the field.

Since the problem has been in the spotlight for several decades, it should be acknowledged by now. Conservators and conservation scientists have been collaborating all this time, hopefully leading to a better understanding on both sides.

The voice of conservation scientists themselves has been missing; thus, the situation seems strangely one-sided. This is perhaps due to conservation scientists finding their ecological slot within the academic world, where cold numbers measure success. “Impact” in the academic vocabulary does not represent any real-life effect but the number of times a publication has been referenced in subsequent publications. This tight circle means that a conservation scientist should worry more about producing as many publications as possible rather than the applicability of the said research.

Conservation scientists are not to blame for the way academia works these days. The problem is primarily acknowledged, and humanities are generally suffering from the natural scientific publication system that values quantity over quality. Scientists are also likely to be used to valuing information for its own sake and letting others take care of the applications. This might work in engineering or the medical sector withextensive economic resources, competence, and workforce. However, it does not work in the conservation sector, which is run by a handful of overworked people leaning towards the humanities.

The most successful projects likely to produce valuable results are carried out as a long-term collaboration between scientists and conservators to solve a specific treatment problem. There are good examples of such collaboration in the desalination field, such as the ODéFA project carried out in France (Guilminot et al. 2012; Kergourlay et al. 2010), or the Rettung vor Dem Rost project in Germany (Schmutzler and Eggert 2010a, 2010c; Schmutzler 2012), to name but a few.

8.2. Obstacles in education

Conservation is a broad subject which makes it challenging to teach. Relevant skills are divided between the entire field of heritage. This is a vast and constantly expanding field that no single individual can master. Developing a course that would prepare the student to treat any object with confidence is impossible.

The answer to this problem has been to divide education into separate fields of study so that relevant skills and theories can be taught to students working with different materials. This approach is a balancing act, however. The more specific the education, the more relevant it is likely to be. At the same time, it gets more expensive as group sizes will be small.

There is pressure to cut funding for education in the current climate. The ageing populations of Europe are putting pressure on political economies, and it is becoming increasingly difficult to fund the Nordic ideal of the welfare state. Maintaining economic growth in a shrinking population is difficult, and growth is an integral part of any capitalistic system. If stagnant or shrinking economies become a permanent phenomenon, it leads to unpredictable and fundamental changes in Nordic societies.

Humanities are especially vulnerable as they do not contribute to economic growth – or at least, they are not considered to do so. On the contrary, humanities are considered an expenditure in the national budget. The return for investment in the heritage industry is prestige, which is a luxury. If the economy suffers, the heritage sector is usually one of the first to suffer funding cuts.

It is no coincidence that the golden age of museum institutions was also the golden age of nationalism. The emerging nation-states depended on heritage institutions to solidify their power. With the emergence of postmodernism and critical heritage studies, the spearhead of research no longer provides nations with the validation they used to provide – on the contrary; they question the relevance of the national myths.

Since this is the case, it can be asked what interest the state has in funding such research. If the heritage sector as we know it was emerging today, it would be very unlikely that national museums would be raised at the city centres next to senates and churches as they were in the 19th century.

Values change slowly, however. This applies both to national structures and the heritage sector. The heritage sector still contributes to the national identity, and nations still feel obliged to fund it. Heritage is very resilient in the face of rational critique. Sudden changes are unlikely, but preparing for slowly diminishing funds across the sector is probably best.

The consequences of this are already felt in the educational system. Teaching specialists like archaeological conservators is expensive. Only a handful are needed yearly in the Nordic countries, so if they should be trained locally, the education price per person will likely climb to an unacceptable level.

The pressure to cut costs drives the education system towards training larger numbers of generalists. This development goes hand in hand with another general trend, which is the increase of emphasis on passive conservation and collections management at the expense of active treatment. The risk with this approach is an erosion of active conservation skills. It also means that the graduated students are less familiar with the current state of research and development in any specialised field of conservation and, thus, more inclined to commit to tradition than progress.

This educational system puts much pressure on conservation institutions and students. If education produces generalists, employers need to train their specialists. Relevant skills need to be acquired through work experience. Practice does not make perfect; practice makes permanent. Perfect practice makes perfect. This is why work experience needs to be supervised and practice reflective (Pye 2001: 173). This process happens at the employer’s expense, naturally making them reluctant to commit to such a system.

If a pupil knows at an early enough stage of their education what field they wish to specialise in, they can try to acquire the relevant skills during their studies through internships, projects, and private studies. It greatly helps if they already have education in the sector they wish to specialise in, such as art history or archaeology. Elizabeth Pye (2001) has even argued that such background should be a qualification criterion for becoming a conservation student. This is understandable but quite ambitious in a political climate where studies are considered to take too long, even without such meandering study paths.

From an archaeological conservator’s perspective, generalising the studies involves the same risk present in any generalised conservation setting: that discourse specific to high art conservation starts to dominate. As stated before, high art has the highest prestige among the different branches of conservation, and we are used to giving it priority in professional settings. However, the scope must be broadened if we want studies to prepare students for the care and treatment of natural history, scientific, or archaeological collections. These collections should not be taken care of as if they were art.

So, archaeological laboratories have a big responsibility if education is saturating the field with art-oriented generalists. Teaching the relevant skills means years of supervised experience and integration into the specifics of archaeological research and collections management equally requires a long process of tight collaboration with professionals taking care of these fields. These processes do not happen by themselves, and if ignored, they could result in a situation where precious time and resources are lost to miscommunication and incompetence.

8.3. Obstacles in daily practice

The situation is further complicated because there is no institution to evaluate and assess the competence and professionalism of conservators. “Conservator” is not a protected professional title in the Nordic countries, and the field is young and underappreciated among academic titles in the heritage field.

Membership in professional organisations, such as the IIC Nordic Group, requires formal education in the field, but no institution monitors one’s competence in the profession. Once an individual has passed their education, they will remain formally qualified, and their professionalism will be judged by their reputation alone.

The heritage sector is the most prominent advocate of its subject. We promote the idea that we preserve the heritage for the entire population, but the truth is that usually, we have the greatest interest in it ourselves. The public does not evaluate our work on the same measures as we do ourselves: they would be doubtful to react to what we would consider maltreatment inside the sector.

This makes the sector, in the lines of a Finnish idiom, “like a goat guarding a cabbage field”. Lack of external interest means we must do our own quality control, but how does one measure the quality of conservation efforts? The lack of universally agreed standards leads to the temptation of defining whatever is taking place in the laboratory as being of high quality.

Conservation is paid by the taxpayer for a purpose, so we must be disciplined and strive for high standards. As there is seldom external pressure for development, this should be internal. There is a risk of stagnation if no questions are asked, as change requires deliberate effort. “Business as usual” tends to result if a laboratory is run on autopilot (Pye 2001: 160).

Change is necessary for development, but it often pushes conservators to their discomfort zones. Deviating from the tried and tested requires one to motivate and reason one’s choices, exposing one to critique. However, it is often forgotten that the standard procedures should be exposed to the same scrutiny as the proposed alternative. Tradition and familiarity with a method are arguments that need to be considered, but they should not be the primary motivation behind any conservation decision.

Here written laboratory master reports, as Appelbaum suggested (2007), could help illuminate the reasoning behind methods regularly used in a laboratory. Critically reviewing the report every few years in light of recent research literature should help keep the practice up to date.

The community that values the objects defines good practice on a case-to-case basis. The conservator needs to actively participate in negotiating the values we are trying to preserve in the material undergoing treatment so that she can positively contribute to the process. Participation is also necessary because other actors cannot be expected to understand conservation processes. So, they are not necessarily fully aware of the consequences of their views. The same applies to the conservator, who needs to be open to understanding what her decisions mean to the other interest parties.

9. References

Al‐Zahrani, Abdulnaser (1999), 'Chloride Ion Removal From Archaeological Iron and ß-FeOOH', Doctoral (University of Wales).

Andersen, Lars Brock (2006), 'Desalination of Archaeological Iron Artefacts after D.C. Mode Hydrogen Plasma Treatment', *Archaeological Metal Finds - From Excavation to Exhibition* (Mannheim, Germany).

Anonymous (2011), 'Model 926 Chloride Analyser Operator's Manual', (Sherwood Scientific Limited), 23.

Appelbaum, Barbara (2007), *Conservation Treatment Methodology* (Butterworth-Heinemann) 437.

Arponen, Aki, et al. (2022), 'Subcritical Fluids in the Conservation of Archaeological Iron Objects: From Experiments to Permanent Practice', in Paul Mardikian, Liisa Näsänen, and Aki Arponen (eds.), *METAL 2022: Interim Meeting of the ICOM-CC Metals Working Group* (Helsinki, Finland: International Council of Museums - Committee for Conservation

The National Museum of Finland), 324.

Avrami, Erica, Mason, Randall, and de la Torre, Marta (eds.) (2000), *Values and Heritage Conservation* (Research on Values of Heritage, Los Angeles, USA: The Getty Conservation Institute) 96.

Bayle, Marine (2015), 'Déchloruration des objects archéologiques ferreux par le processus de stabilisation subcritique - Caractérisations physico-chimiques des systèmes transformés', Doctoral Thesis (Université Pierre et Marie Curie).

Bayle, Marine, et al. (2016), 'Corrosion product transformations in alkaline baths under pressure and high temperature: The sub-critical stabilisation of marine iron artefacts stored under atmospheric conditions', *Materials and Corrosion,* 67 (2), 190-99.

Beaudoin, A., et al. (1995), 'Corrosion d'objets archéologiques en fer après déchloruration par la méthode au sulfite alcalin: caractérisation physico-chimique et rétraitement électrochimique ', in Ian D. MacLeod, Stéphane L. Pennec, and Luc Robbiola (eds.), *International conference on metals conservation* (Semur-en-Auxois, France: James & James), 170-77.

Berducou, Marie (1996), 'Introduction to Modern Archaeological Conservation', in Nicholas Stanley Price, M. Kirby Jr. Talley, and Alessandra Melucco Vaccaro (eds.), *Historical and philosophical issues in the conservation of cultural heritage* (Readings in conservation; Los Angeles, United States: The Getty Conservation Institute), 248-59.

Bertholon, Régis (2001), 'To get rid of the crust or not : emergence of the idea of 'original surface' in the conservation of metal archaeological objects in the first half of the 20th century', in Andrew Oddy and Sandra Smith (eds.), *Past Practice - Future Prospects* (British Museum Occasional Papers, 145; London, United Kingdom: British Museum Press), 5-11.

Bier, Axel (2018), 'Electrochemistry - Theory and Practice', (Edition 3 edn.: Hach).

Brockbank, Anne and McGill, Ian (1998), *Facilitating Reflective Learning in Higher Education* (Buckingham, United Kingdom: Society for Research into Higher Education and the Open University Press).

Burke, Donald (2018), 'Ancient Violence / Modern Violence: The Negative Legacy of the Viking Age', *Weaving War: New perspectives on violence and society in the Viking Age* (Oslo, Norway).

Camman, Karl (1979), *Working with Ion-Selective Electrodes: Chemical Laboratory Practice*, eds F.L. Boschke, et al., trans. Albert H. Schroeder (2 edn., Anleitungen für die chemische Laboratoriumspraxis; Berlin, Heidelberg, New York: Springer-Verlag) 226.

Caple, Chris (2000), *Conservation Skills: Judgement, method and decision making* (London, United Kingdom: Routledge).

--- (2006), *Objects : reluctant witnesses to the past* (New York, USA: Routledge).

Carlin, Worth, Keith, Donald, and Rodriguez, Juan (2001), 'Less Is More: Measure of Chloride Removal Rate from Wrought Iron Artifacts during Electrolysis', *Studies in Conservation,* 46 (1), 68-76.

Coelho, J. C., et al. (2014), 'The efficiency of electrochemical methods for the removal of chloride ions from iron marine archaeological objects: A comparative study', *Materials and Corrosion,* 65 (1), 38-44.

Comensoli, Lucrezia, et al. (2017), 'Use of bacteria to stabilize archaeological iron', *Applied and Environmental Microbiology,* 83 (9), e03478-16.

Comensoli, Lucrezia, et al. (2019), 'The Potential of Microorganisms for the Conservation-Restoration of Iron Artworks', in Claudia Chemello, Laura Brambilla, and Edith Joseph (eds.), *METAL 2019: Interim Meeting of the ICOM-CC Metals Working Group* (Neuchâtel, Switzerland: International Council of Museums - Committee for Conservation & Haute Ecole Arc Conservation-restauration), 243-49.

Costain, Charles G (2000), 'Evaluation of storage solutions for archaeological iron', *Journal of the Canadian Association for Conservation,* 25, 11-20.

Costain, Charlie and Logan, Judith (1985), 'Survey of iron artefacts from Red Bay, Labrador to assess the effectiveness of various iron treatments', *ICOM Committee for Conservation Metals Working Group newsletter,* 22 (1), 8-9.

De la Torre, Marta (ed.), (2002), *Assessing the Values of Cultural Heritage: Research Report.* (Research on Values of Heritage).

de Viviés, Philippe (2022), 'Sustainability from a Private Practice Perspective', *METAL 2022: Interim Meeting of the ICOM-CC Metals Working Group* (Helsinki, Finland).

de Viviesa, Philippe, et al. (2007), 'Transformation of akaganeite in archaeological iron artefacts using subcritical treatment', *a. a,* 35 (30), e2s.

Degrigny, Christian (2004), 'Altération et conservation des objets métalliques issuus de fouilles sous marines', in Salvatore Siano (ed.), *Studio e Conservazione di Manufatti Archeologici* (Firenze, Italy: Nardini Editore), 243-74.

Degrigny, Christian and Lacoudre, Noël (1999), 'Les techniques électrolytiques - Nouvelles technologies dans la restauration des métaux archéologiques', in H. Meyer-Roudet (ed.), *A la recherche du metal perdu* (Paris, France: Editions Errance), 114-27.

Drews, Michael J., et al. (2004), 'A study of the analysis and removal of chloride in iron samples from the Hunley', in John Ashton and David Hallam (eds.), *International Conference on Metals Conservation 2004* (Canberra, Australia: National Museum of Australia), 247-60.

Drews, Michael J., et al. (2013), 'The application of subcritical fluids for the stabilization of marine archaeological iron', *Studies in Conservation,* 58 (4), 314-25.

E.C.C.O. (2002a), *Professional Guidelines I. The Profession.* (European Confederation of Conservator-Restorers‘ Organisations) 4.

--- (2002b), *Professional Guidelines III. Education* (European Confederation of Conservator-Restorers' Organisations) 2.

--- (2002c), *Professional Guidelines II. Code of Ethics* (European Confederation of Conservator-Restorers‘ Organisations) 4.

Edson, Gary (ed.), (1997), *Museum ethics* (London, Great Britain: Routledge) 308.

Emmerson, Nicola J., et al. (2022), 'The Effect of Synthesis Routes on the Ability of Akaganeite to Corrode Iron', in Paul Mardikian, Liisa Näsänen, and Aki Arponen (eds.), *METAL 2022: Interim Meeting of the ICOM-CC Metals Working Group* (Helsinki, Finland: International Council of Museums – Committee for Conservation (ICOM-CC) and The National Museum of Finland), 240-47.

English Heritage (2008) *Investigative Conservation* [online text], English Heritage Publishing <https://content.historicengland.org.uk/images-books/publications/investigative-conservation/investigative-conservation.pdf/>

Federspiel, Beate (2001), 'The Definition of the Conservation Profession and its Field of Operation: Issues in the 21st Century', in Andrew Oddy and Sandra Smith (eds.), *Past Practice - Future Prospects* (British Museum Occasional Papers, 145; London, United Kingdom: British University Press), 75-79.

Fenn, J. D. and Foley, K. (1975), 'Passivation of Iron', *Studies in Conservation,* 20 (sup1), 195-98.

Ferguson, Robert (1992), 'Trends in conservation education and training: War of words or words of war?', *Museum Management and Curatorship,* 11 (4), 411-18.

Frog and Ahola, Joonas (2014), 'Approaching the Viking Age in Finland - An Introduction', in Clive Tolley, Frog, and Joonas Ahola (eds.), *Fibula, Fabula Fact - The Viking Age In Finland* (Studia Fennica; Helsinki, Finland: Finnish Literature Society), 21-68.

Ganiaris, Helen, Barham, Liz, and Goodman, Liz (2012), 'Great expectations: a review of iron from waterlogged contexts from London sites excavated in the 1980s and 1990s', *Journal of the Institute of Conservation,* 35 (1), 3-13.

Gilberg, Mark R. (1985), 'The Storage of Archaeological Iron Under Deoxygenated Conditions', *ICOM Committee for Conservation Metals Working Group newsletter,* 1, 3.

--- (1987), 'Friedrich Rathgen: The Father of Modern Archaeological Conservation', *Journal of the American Institute for Conservation,* 26 (2), 105-20.

Gilberg, Mark R. and Seeley, Nigel J. (1982), 'The Alkaline Sodium Sulphite Reduction Process for Archaeological Iron: A Closer Look', *Studies in Conservation,* 27 (4), 180-84.

Gilberg, Mark R. and Vivian, Dan (2001), 'The Rise of Conservation Science in Archaeology (1830-1930)', in Andrew Oddy and Sandra Smith (eds.), *Past Practice - Future Prospects* (British Museum Occasional Papers, 145; London, United Kingdom: British Museum Press).

González-Pereyra, Néstor, Näsänen, Liisa, and Cretté, Stéphanie (2013), 'From Rivets to Composites - Ten Years of Subcritical Research', in Ewan Hyslop, et al. (eds.), *Interim Meeting of the ICOM-CC Metal Working Group* (Edinburgh, United Kingdom: Historic Scotland), 201-06.

Gonzalez, Nestor, et al. (2007), 'The effects of cathodic polarization, soaking in alkaline solutions and subcritical water on cast iron corrosion products', in Christian Degrigny (ed.), *Interim Meeting of the ICOM-CC Metal Working Group* (Amsterdam, Netherlands: ICOM-CC Metal WG), 17-21.

González, Nestor G., et al. (2004), 'Hunting Free and Bound Chloride in the Wrought Iron Rivets from the American Civil War Submarine H. L. Hunley', *Journal of the American Institute for Conservation,* 43 (2), 161-74.

González, Néstor G., et al. (2013), 'The use of subcritical fluids for the stabilisation of archaeological iron: an overview', in P. Dillmann, et al. (eds.), *Corrosion and conservation of cultural heritage metallic artefacts* (EFC; Cambridge, United Kingdom: Woodhead Publishing), 434-65.

Greiff, Susanne and Bach, Detlef (2000), 'Eisenkorrosion und Natriumsulfitentsalzung: Therorie und Praxis', *Arbeitsblätter für Restauratoren,* 33 (2), 319-39.

Guilminot, Elodie, et al. (2012), 'Influence of crucial parameters on the dechlorination treatments of ferrous objects from seawater', *Studies in Conservation,* 57 (4), 227-36.

Hamilton, Donny L. (2020), 'Methods of Conserving Underwater Archaeological Material Culture', (updated 1.3.2010) <https://nautarch.tamu.edu/CRL/conservationmanual/>, accessed 7.1.

Häyhä, H (1999), 'The History of Iron Protection. Description of Materials and the Evaluation of Their Properties', in Rikhard Hordal and Tannar Ruuben (eds.), *Description of Materials and Evaluation of their Properties. The Baltic Nordic Conference on Conserved and Restored Works of Art* (Tallinn, Estonia: Conservation Centre Kanut), 117-21.

Hjelm-Hansen, Nils, et al. (1992), 'Electrochemical monitoring of archeological iron artifacts during treatment', *3a Conferenza internazionale sulle prove non distruttive, metodi microanalitici e indagini ambientali per lo studio e la conservazione delle opere d'arte: Viterbo 4-9 ottobre 1992= 3rd International Conference on Nondestructive Testing, Microanalytical Methods and Environment Evaluation for Study and Conservation of Works of Art* (Viterbo, Italy: Italian Society for Nondestructive Testing, Brescia, Italy), 359-74.

Hjelm-Hansen, Nils, et al. (1993), 'Electrochemical assessment and monitoring of stabilisation of heavily corroded archaeological iron artefacts', *Corrosion Science,* 35 (1), 767-74.

ICOM-CC (2023), 'Terminology for conservation', <https://www.icom-cc.org/en/terminology-for-conservation>, accessed 22 March.

ICOM (2004), *ICOM Code of Ethics* (Paris, France: International Council of Museums).

ICOMOS (1931), *The Athens Charter for the Restoration of Historic Monuments* (International Council on Monuments and Sites).

--- (1964), *The Venice Charter: International Charter for the Conservation and Restoration of Monuments and Sites.* (International Council on Monuments and Sites).

--- (1995), *Nara Document, Nara Conference on Authenticity.* (Paris, France: Unesco).

ICOMOS, Asutralia (1979), *The Burra Charter: the Australia ICOMOS Charter for the Conservation of Places of Cultural Significance*.

Jakobsen, Tove (1988), 'Iron Corrosion Theories and the Conservation of Archaeological Iron Objects in the 19th Century with an Emphasis on Scandinavian and German Sources', in V. Daniels (ed.), *Early Advances in Conservation* (British Museum Occasional Papers, 65; London, United Kingdom: British Museum Press), 51-58.

Javier, Peréz de Cuéllar (1995), *Our Creative Diversity: Report of the World Commission on Culture and Development* (Paris, France: Unesco Publishing).

Joseph, Edith, et al. (2022), 'Microbial Stabilization of Archaeological Iron Objects', in Liisa Näsänen, Paul Mardikian, and Aki Arponen (eds.), *METAL 2022: Interim Meeting of the ICOM-CC Metals Working Group* (Helsinki, Finland: International Council of Museums - Committee for Conservation

The National Museum of Finland), 35-39.

Kavanagh, Gaynor (1991), 'The Museums Profession and the Articulation of Professional Self-Consciousness', in Gaynor Kavanagh (ed.), *The Museums Profession: Internal and External Relations* (Leicester Museum Studies; Leicester, United Kingdom: Leicester University Press), 37-55.

Keene, Suzanne S. (1987), 'Desalination Treatments: a Comparison from a Conservator's Point of View', *Jern, Fremstilling, Nedbrydning og Bevaring. Fortryk af Forelæsninger til Nordisk Videreutdannelse af Konservatorer. København, 17-28 august 1987* (; Copenhagen, Denmark: Nationalmuseet), 1-6.

--- (1991), 'Real-time survival rates for treatments of archaeological iron', in David A. Scott, Jerry Podany, and Brian B. Considine (eds.), *Ancient & Historic Metals, Conservation and Scientific Rerearch* (Los Angeles, USA: Getty Conservation Institute), 249-64.

--- (2002) *Managing Conservation in Museums* [online text], Taylor and Francis <http://ebookcentral.proquest.com/lib/gu/detail.action?docID=300571>

Keene, Suzanne S. and Orton, Clive (1985), 'Stability of treated archaeological iron: an assessment', *Studies in Conservation,* 30 (3), 136-42.

Kergourlay, Florian, et al. (2010), 'Influence of corrosion products nature on dechlorination treatment: case of wrought iron archaeological ingots stored 2 years in air before NaOH treatment', *Corrosion Engineering, Science and Technology,* 45 (5), 407-13.

Knight, Barry (1990), 'A review of the corrosion of iron from terrestrial sites and the problem of post ‐ excavation corrosion', *The Conservator,* 14 (1), 37-43.

--- (1995), 'The stabilisation of archaeological iron: past, present and future', in Ian D. MacLeod, Stéphane L. Pennec, and Luc Robbiola (eds.), *International Conference on Metals Conservation* (Semur-en-Auxois, France: James & James), 36-40.

Koh, Yang Sook and Skogstad, Hilde (2015), 'Urlakning av arkeologisk järn: Masskonservering av gotländska fynd', *Meddelelser om Konservering,* 2015, 25-37.

Kølvraa, Christoffer (2019), 'Embodying ‘the Nordic race’: imaginaries of Viking heritage in the online communications of the Nordic Resistance Movement', *Patterns of Prejudice,* 53 (3), 270-84.

Kostet, Juhani (2023), 'Rakentavaa keskustelua museoiden kokoelmista tarvitaan', [Blog], <http://blogi.nba.fi/2013/rakentavaa-keskustelua-kokoelmista-tarvitaan>, accessed 14 April.

Krause, Edward (1882), 'Ein neues Verfahren zur Conservirung der Eisen-Alterthümer', *Zeitschrift für Ethnologie,* 14, 533-38.

Kuhn, Charlotte Friederike, et al. (2011), 'Another base, another solvent? Desalinating iron finds with tetramethylammonium hydroxide solution', *e-Preservation Science,* 8, 81-85.

Lagerstedt, John; Roiha, Johanna (2020), 'HELSINKI, Kruunuhaka, Mariankatu 3. Vanhan tulli- ja pakkahuoneen arkeologinen kaivaus ja valvonta 2018–2019. Tutkimusraportti', (Helsinki, Finland: Finnish Heritage Agency).

Loeper-Attia, Marie-Anne and Weker, Wladyslaw Henryk (1995), 'Déchloruration d'Objets Archéologiques en Fer par la Méthode du Sulfite Alcalin à l'IRRAP', in Ian D. MacLeod, Stéphane L. Pennec, and Luc Robbiola (eds.), *International Conference of Metals Conservation* (Semur-en-Auxois, France: James & James), 162-66.

Lowenthal, David (2015), *The past is a foreign country - revisited* (Cambridge, United Kingdom: Cambridge University Press) 660.

MacLeod, Ian Donald (1984), 'Conservation, Applied Science And Why Treatments Must Be Monitored', *AICCM Bulletin,* 10, 19-41.

--- (1987), 'Conservation of Corroded Copper Alloys: A Comparison of New and Traditional Methods for Removing Chloride Ions', *Studies in Conservation,* 32 (1), 25-40.

Manninen, Mikael A. (2014), 'Museovirasto ja arkeologiset kokoelmat. Missä mennään? - Keskustelutilaisuus Tieteiden talolla Helsingissä 26.2.2014', *Muinaistutkija,* (2), 6.

Mardikian, Paul, et al. (2009), 'New perspectives regarding the stabilization of terrestrial and marine archaeological iron', in Michael McCarthy (ed.), *Iron, Steel & Steamship Archaeology* (Special publication (Australasian Institute for Maritime Archaeology); 15, Special Publication (Australian National Centre of Excellence for Maritime Archaeology); No. 13.; Fremantle, Melbourne & Sydney - Australia: Australian National Centre of Excellence for Maritime Archaeology), 113-18.

Mason, Randy (ed.), (1998), *Economics and Heritage Conservation: A Meeting Organized by the Getty Conservation Institute, December 1998, Getty Center, Los Angeles* (Research on the Values of Heritage, Los Angeles, United States: Getty Conservation Institute).

Matthiesen, Henning (2013), 'Oxygen monitoring in the corrosion and preservation of metallic heritage artefacts', in P. Dillmann, et al. (eds.), *Corrosion and Conservation of Cultural Heritage Metallic Artefacts* (EFC series: Woodhead Publishing), 368-91.

Matthiesen, Henning, et al. (2022), 'Natural Conservation of Archaeological Iron', in Liisa Näsänen, Paul Mardikian, and Aki Arponen (eds.), *METAL 2022: Interim Meeting of the ICOM-CC Metals Working Group* (Helsinki, Finland: International Council of Museums - Committee for Conservation

The National Museum of Finland), 16-24.

Mikhelson, Konstantin N. (2013), *Ion-Selective Electrodes*, eds B. Carpenter, et al. (Lecture Notes in Chemistry; Heidelberg, Germany: Springer) 162.

Mökkönen, Teemu and Manninen, Mikael A. (2013), 'Arvokas tietopankki', *Savon Sanomat,* 2.5.2013.

Muñoz Viñas, Salvador (2005), *Contemporary Theory of Conservation* (Oxford, Great Britain: Elsevier Butterworth-Heinemann).

Näsänen, Liisa M. E., et al. (2013), 'The applicability of subcritical fluids to the conservation of actively corroding iron artifacts of cultural significance', *The Journal of Supercritical Fluids,* 79, 289-98.

Neff, Delphine, et al. (2005), 'Corrosion of iron archaeological artefacts in soil: characterisation of the corrosion system', *Corrosion Science,* 47 (2), 515-35.

Neff, Delphine, et al. (2006), 'Corrosion of iron archaeological artefacts in soil: Estimation of the average corrosion rates involving analytical techniques and thermodynamic calculations', *Corrosion Science,* 48 (10), 2947-70.

Neff, Delphine, et al. (2004), 'Structural characterization of corrosion products on archaeological iron: an integrated analytical approach to establish corrosion forms', *Journal of Raman Spectroscopy,* 35 (8-9), 739-45.

Norlander, Åsa and Mattsson, Einar (1996), 'Bevarande av arkeologiskt järn efter utgrävning', (Konserveringstekniska studier; Stockholm, Sweden: Riksantikvarieämbetet).

North, Neil A. (1987), 'Conservation of metals', in Colin Pearson (ed.), *Conservation of Marine Archaeological Objects* (Butterworths Series in Conservation and Museology; Bodmin, United Kingdom: Butterworth & Co.), 207-52.

North, Neil A. and Pearson, Colin (1975), 'Alkaline sulfite reduction treatment of marine iron', *Icom committee for conservation. 4th triennial meeting, Venice, 13-18 October. Preprints* (Venice, Italy: Bouwcentrum (Impr.) [for] ICOM), 75133-1-33-14.

--- (1978b), 'Washing Methods For Chloride Removal From Marine Iron Artifacts', *Studies in Conservation,* 23 (4), 174-86.

--- (1978c), 'Recent advances in the stabilisation of marine iron', in Robert M. Organ, Elżbieta Maria Nosek, and Janusz Lehmann (eds.), *Conservation of iron objects found in a salty environments* (Warsaw, Poland: Historical monuments documentation centre), 26-38.

Oddy, William Andrew (1996), 'The Forbes Prize Lecture 1996', *IIC Bulletin,* 5, 5.

Oddy, William Andrew and Carroll, Sara (1999), *Reversibility : does it exist?* (Occasional paper; London: British Museum).

Organ, Robert M. (1955), 'The washing of treated bronzes', *The Museums Journal,* 55 (5), 112-19.

Pearce, Susan M. (1992), *Museums, Objects and Collections: A Cultural Study* (Leicester and London, Great Britain: Leicester University Press) 296.

Pearson, Colin (1981), 'Conservation of the underwater heritage', in Colin Martin (ed.), *Protection of the underwater heritage* (Protection of the cultural heritage: technical handbooks for museums and monuments; Paris, France: UNESCO), 78-133.

Pelé, Charlène, Lemoine, Stéphane, and Guilminot, Elodie (2010), 'Evolution of pH in the Solutions of Dechlorination', in Britta Schmutzler and Gerhard Eggert (eds.), *Archaeological Iron Conservation Colloquium 2010* (Stuttgart, Germany).

Plenderleith, Harold James (1956), *The Conservation of Antiquities and Works of Art: Treatment, Repair, and Restoration* (1 edn.; Oxford, Great Britain: Oxford University Press).

Plenderleith, Harold James and Werner, Alfred Emil Anthony (1971), *The Conservation of Antiquities and Works of Art: Treatment, Repair and Restoration* (2 edn.; London: Oxford University Press) 394.

Pye, Elizabeth M. (2001), *Caring for the past: Issues in conservation for archaeology and museums* (London, United Kingdom: James & James Ltd.) 232.

Rathgen, Friedrich (1898), *Die Konservierung von Alterthumsfunden* (W. Spemann).

--- (1905), *The Preservation of Antiquities: A Handbook for Curators*, trans. Geroge A. Auden and Harold A. Auden (Cambridge, United Kingdom: Cambridge, University Press).

Reguer, Solenn, et al. (2005), 'Local and structural characterisation of chlorinated phases formed on ferrous archaeological artefacts by µXRD and µXANES', *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms,* 240 (1), 500-04.

Réguer, Solenn, Dillmann, Philippe, and Mirambet, Francois (2007), 'Buried iron archaeological artefacts: Corrosion mechanisms related to the presence of Cl-containing phases', *Corrosion Science,* 49 (6), 2726-44.

Réguer, Solenn, et al. (2015), 'Iron corrosion in archaeological context: Structural refinement of the ferrous hydroxychloride β-Fe2(OH)3Cl', *Corrosion Science,* 100, 589-98.

Rimmer, Melanie (2010), 'Investigating the treatment of chloride-infested archaeological iron objects', Doctoral (Cardiff University (United Kingdom)).

Rimmer, Melanie and Wang, Quanyu (2010), 'Assessing the effects of alkaline desalination treatments for archaeological iron using scanning electron microscopy', *British Museum Technical Research Bulletin,* 4, 79-86.

Rimmer, Melanie, Watkinson, David, and Wang, Quanyu (2012), 'The efficiency of chloride extraction from archaeological iron objects using deoxygenated alkaline solutions', *Studies in Conservation,* 57 (1), 29-41.

--- (2013), 'The impact of chloride desalination on the corrosion rate of archaeological iron', *Studies in Conservation,* 58 (4), 326-37.

Rinuy, Anne (1979), 'Vergleichende Untersuchungen zur Entsalzung von Eisenfunden', *Arbeitsblätter für Restauratoren* 1979 (1), 130-40.

Rinuy, Anne and Schweizer, Francois (1980), 'Application of the alkaline sulphite treatment to archaeological iron: a comparative study of different desalination methods', in RW Clarke and SM Blackshaw (eds.), *Conservation of iron* (Maritime monographs and reports, 53; Greenwitch, United Kingdom: National maritime museum), 44-49.

--- (1982), 'Entsalzung von eisenfunden mit alkalischer sulfitlösung', *Arbeitsblätter für restauratoren,* 1982 (1), 160-74.

Roche, Kimberly, et al. (2022), 'Standardizing Acid Digestion Methodology to Determine the Chloride Content of Ferrous Corrosion Samples', in Paul Mardikian, Liisa Näsänen, and Aki Arponen (eds.), *METAL 2022: Interim Meeting of the ICOM-CC Metals Working Group* (Helsinki, Finland: International Council of Museums – Committee for Conservation (ICOM-CC) and The National Museum of Finland), 358.

Rundle, Chris C. (2023), 'Beginners Guide to ISE Measurement. Chapter 3.', <https://www.nico2000.net/Book/Guide4.html>, accessed 18 May.

--- (2023), 'Standard Addition & Sample Addition methods for Ion Selective Electrodes.', <https://www.nico2000.net/datasheets/staddl.html>, accessed 23.5.

Rundle, Chris C. and Cui, Yiying (2022), 'Calculations for Double Standard Addition measurements with Ion Selective Electrodes', <https://www.nico2000.net/datasheets/staddncalcs.xls>, accessed 23 May.

Saheb, Mandana, et al. (2013), 'Long-term anoxic corrosion of iron', in Philippe Dillmann, et al. (eds.), *Corrosion and conservation of cultural heritage metallic artefacts* (EFC, 65; Cambridge, United Kingdom: Woodhead Publishing), 260-84.

Scheiner, Tereza Cristina (1997), 'Museum ethics and the environment: In search of a common virtue', in G. Edson (ed.), *Museum Ethics* (London, Great Britain: Routledge), 178-86.

Schmidt-Ott, Katharina and Oswald, Niklaus (2006a), 'Alkaline Sulfite Desalination - Tips and Tricks', *Archaeological Metal Finds - From Excavation to Exhibition* (Mannheim, Germany).

--- (2006b), 'Neues zur Eisenentsalzung mit alkalischem Sulfit', *Beiträge zur Erhaltung von Kunst-und Kulturgut,* (2), 126-34.

Schmidt-Ott, Katharina, et al. (2017), 'Picturing the bad guys: Application of neutron tomography and image processing to assess dechlorination methods for archaeological iron', *ICOM Committee for Conservation 18th Triennial Meeting* (Copenhagen, Denmark: Pulido & Nunes; ICOM Committee for Conservation).

Schmutzler, Britta (2006), 'Investigations into the alkaline sulfite treatment for conservation of large quantities of archaeological iron objects', *Archäologische Metallfunde* (Mannheim, Germany: ICOM-CC).

--- (2012), 'Rettung vor dem Rost', *Die Weiterentwicklung der Eisenentsalzung nach der Alkali-Sulfit-Methode zur Erhaltung großer Fundmengden* (Internationale Archäologie; Rahden, Germany: Verlag Marie Leidorf GmbH).

Schmutzler, Britta and Ebinger-Rist, Nicole (2008), 'The conservation of iron objects in archaeological preservation – Application and further development of alkaline sulphite method for conservation of large quantities of iron finds', *Materials and Corrosion,* 59 (3), 248-53.

Schmutzler, Britta and Eggert, Gerhard (2010a), 'Chloride calamities: assessment of residual chloride analysis to compare iron desalination methods', in Paul Mardikian, et al. (eds.), *Interim Meeting of the ICOM-CC Metal Working Group* (Charleston, SC, USA: Clemson University), 11-15.

--- (2010b), 'The Chloride Left Behind: (Dis)solving an Analytical Problem', *Archaeological Iron Conservation Colloquium 2010* (Stuttgart, Germany).

--- (2010c), 'Simplifying Sodium Sulphite Solutions - The DBU-Project "Rettung vor dem Rost"', in Britta Schmutzler and Gerhard Eggert (eds.), *Archaeological Iron Conservation Colloquium 2010* (Stuttgart, Germany).

Schmutzler, Britta, Revay, Zsolt, and Stieghorst, Christian (2019), 'Desalination of Archaeological Iron Objects: Comparing the Effectiveness of Sodium Hydroxide Treatments', in Claudia Chemello, Laura Brambilla, and Edith Joseph (eds.), *METAL 2019: Interim Meeting of the ICOM-CC Metals Wroking Group* (Neuchâtel, Switzerland: International Council of Museums - Committee for Conservation & Haute Ecole Arc Conservation-restauration), 250-56.

Scott, David A. and Eggert, Gerhard (2009), *Iron and steel in art : corrosion, colorants, conservation* (London, United Kingdom: Archetype Publications).

Sease, Catherine (1978), 'Benzotriazole: A Review for Conservators', *Studies in Conservation,* 23 (2), 76-85.

Selwyn, Lyndsie (2001), 'Analysis of the chloride ion concentration in aqueous solutions by potentiometric titration', *Research report* (Ottawa, Canada: Canadian Conservation Institute).

--- (2004), 'Overview of archaeological iron: the corrosion problem, key factors affecting treatment, and gaps in current knowledge', in John Ashton and David Hallam (eds.), *International Conference on Metals Conservation* (Canberra, Australia: National Museum of Australia), 294-306.

Selwyn, Lyndsie and Logan, Judith (1993), 'Stability of treated iron: a comparison of treatment methods', in Janet Bridgland (ed.), *ICOM Committee for Conservation Triennial Meeting (10)* (2; Washington, DC, USA: International Council of Museums Committee for Conservation), 803-07.

Selwyn, Lyndsie and Argyropoulos, Vasilike (2005), 'Removal of Chloride and Iron Ions from Archaeological Wrought Iron with Sodium Hydroxide and Ethylenediamine Solutions', *Studies in Conservation,* 50 (2), 81-100.

--- (2006), 'Chlorine determination in archaeological wrought iron by instrumental neutron activation analysis', *Journal of the Canadian Association for Conservation,* 31, 3-12.

Selwyn, Lyndsie, Sirois, P. Jane, and Argyropoulos, Vasilike (1999), 'The corrosion of excavated archaeological iron with details on weeping and akaganéite', *Studies in Conservation,* 44 (4), 217-32.

Selwyn, Lyndsie, McKinnon, W. Ross, and Argyropoulos, Vasilike (2001), 'Models for Chloride Ion Diffusion in Archaeological Iron', *Studies in Conservation,* 46 (2), 109-20.

Semczack, Carl M (1977), 'A comparison of chloride tests', *Studies in conservation,* 22 (1), 40-41.

Sörlin, S. (2001), 'The trading zone between articulation and preservation: production of meaning in landscape history and the problems of heritage decision making', in W.E Krumbein, et al. (eds.), *Durability and Change. The Science, Responsibility, and Cost of Sustaining Cultural Heritage* (Chichester, Great Britain: John Wiley and Sons), 47-59.

Sörling, Erik (1924), 'Konservering av järn', *Fornvännen - Journal of Swedish Antiquarian Research,* 1924 (19), 17.

Spiteri, L. and Degrigny, Christian (2004), 'Electrochemical monitoring of marine iron artefacts during their storage / stabilisation in alkaline solutions ', in John Ashton and David Hallam (eds.), *International Conference on Metals Conservation 2004* (Canberra, Australia: National Museum of Australia), 315-31.

Ståhl, Kenny, et al. (2003), 'On the akaganéite crystal structure, phase transformations and possible role in post-excavational corrosion of iron artifacts', *Corrosion Science,* 45 (11), 2563-75.

Sullivan, Kathleen, McKinnon, Ross W, and Selwyn, Lyndsie (2013), 'Carbon dioxide absorption in alkaline treatment solutions for archaeological iron', in E. Hyslop, et al. (eds.), *Interim meeting of the ICOM-CC Metal Working Group* (Edinburgh, United Kingdom: Historic Scotland), 77-84.

Tallavaara, Miikka, et al. (2010), 'How flakes shatter: a critical evaluation of quartz fracture analysis', *Journal of Archaeological Science,* 37 (10), 2442-48.

Ternisien, V., et al. (2013), 'Evaluating subcritical alkaline fluids for a batch stabilisation of iron artefacts from the H.L. Hunley submarine (1864)', in E. Hyslop, et al. (eds.), *Interim meeting of the ICOM-CC Metal Working Group* (Edinburgh, United Kingdom: Historic Scotland), 193-200.

Thickett, David (2022), 'Using Epidemiology to Validate Scientific Results for Complex Situations', in Paul Mardikian, Liisa Näsänen, and Aki Arponen (eds.), *METAL 2022: Interim Meeting of the ICOM-CC Metals Working Group* (Helsinki, Finland: International Council of Museums – Committee for Conservation (ICOM-CC) and The National Museum of Finland), 253-60.

Turgoose, Stephen (1982), 'Post-excavation changes in iron antiquities', *Studies in Conservation,* 27 (3), 97-101.

--- (1985), 'The corrosion of archaeological iron during burial and treatment', *Studies in Conservation,* 30 (1), 13-18.

--- (1989), 'Structure, composition and deterioration of unearthed iron objects ', in Shigeo Aoki (ed.), *Current problems in the conservation of metal antiquities: thirteenth international symposium on the the conservation and restoration of cultural property, 4-6 October 1989, Tokyo, Japan* (Tokyo, Japan: Tokyo National Research Institute of Cultural Properties), 35-53.

Vuorio, Kaija, (2013), 'Museoviraston pääjohtaja: Arkeologiset löydöt takaisin kotiseuduilleen'. <https://www.savonsanomat.fi/paikalliset/3280001>

Wang, Quanyu, et al. (2008), 'Evaluation of methods of chloride ion concentration determination and effectiveness of desalination treatments using sodium hydroxide and alkaline sulphite solutions', *The Conservator,* 31 (1), 67-74.

Watkinson, David (1980), 'An assessment of lithium hydroxide and sodium hydroxide treatments for archaeological ironwork', in R Clarke and S Blackshaw (eds.), *Conservation of iron* (Maritime monographs and reports, 53; Greenwich: National maritime museum), 28-43.

--- (1996), 'Chloride extraction from archaeological iron: comparative treatment efficiencies', *Studies in Conservation,* 41 (sup1), 208-12.

--- (2010), 'Measuring effectiveness of washing methods for corrosion control of archaeological iron: problems and challenges', *Corrosion Engineering, Science and Technology,* 45 (5), 400-06.

Watkinson, David and Lewis, Mark RT (2004), 'The role of ßFeOOH in the corrosion of archaeological iron', *Materials issues in art and archaeology* (Materials Research Society symposium proceedings, 852; Boston, Massachusetts, USA: Materials Research Society), 103-14.

Watkinson, David and Lewis, Mark T. (2005), 'Desiccated Storage of Chloride-Contaminated Archaeological Iron Objects', *Studies in Conservation,* 50 (4), 241-52.

Watkinson, David and Al ‐ Zahrani, Abdulnaser (2008), 'Towards quantified assessment of aqueous chloride extraction methods for archaeological iron: De ‐ oxygenated treatment environments', *The Conservator,* 31 (1), 75-86.

Watkinson, David and Lewis, Mark R. T. (2011), 'The Role of βFeOOH in the Corrosion of Archaeological Iron', *MRS Proceedings,* 852.

Watkinson, David and Rimmer, Melanie B. (2013), 'Quantifying effectiveness of chloride desalination treatments for archaeological iron using oxygen measurement', in E. Hyslop, et al. (eds.), *Interim meeting of the ICOM-CC Metal Working Group* (Edinburgh, United Kingdom: Historic Scotland), 95-102.

Watkinson, David, Rimmer, Melanie B., and Kergourlay, Florian (2013), 'Alkaline desalination techniques for archaeological iron', in Philippe Dillmann, et al. (eds.), *Corrosion and Conservation of Cultural Heritage Metallic Artefacts* (EFC series: Woodhead Publishing), 407-33.

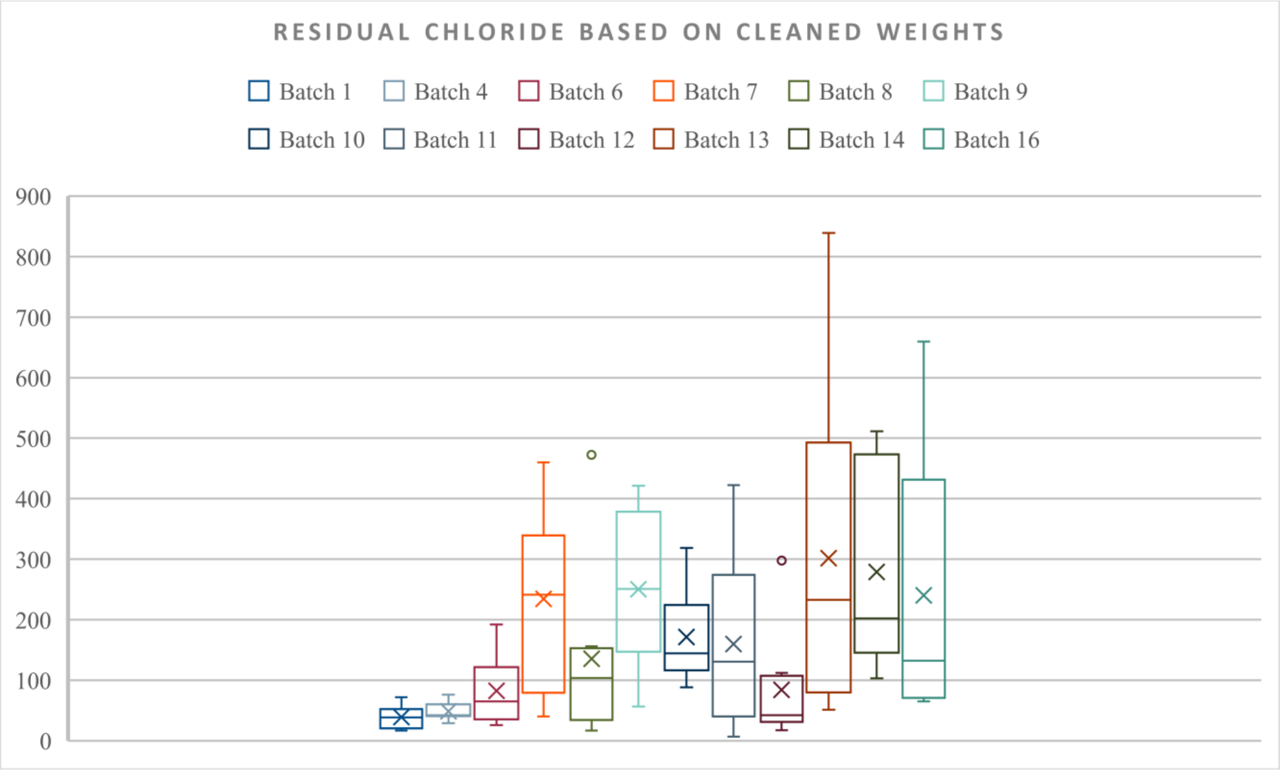
Watkinson, David, et al. (2014), 'The Use of Neutron Analysis Techniques for Detecting The Concentration And Distribution of Chloride Ions in Archaeological Iron', *Archaeometry,* 56 (5), 841-59.

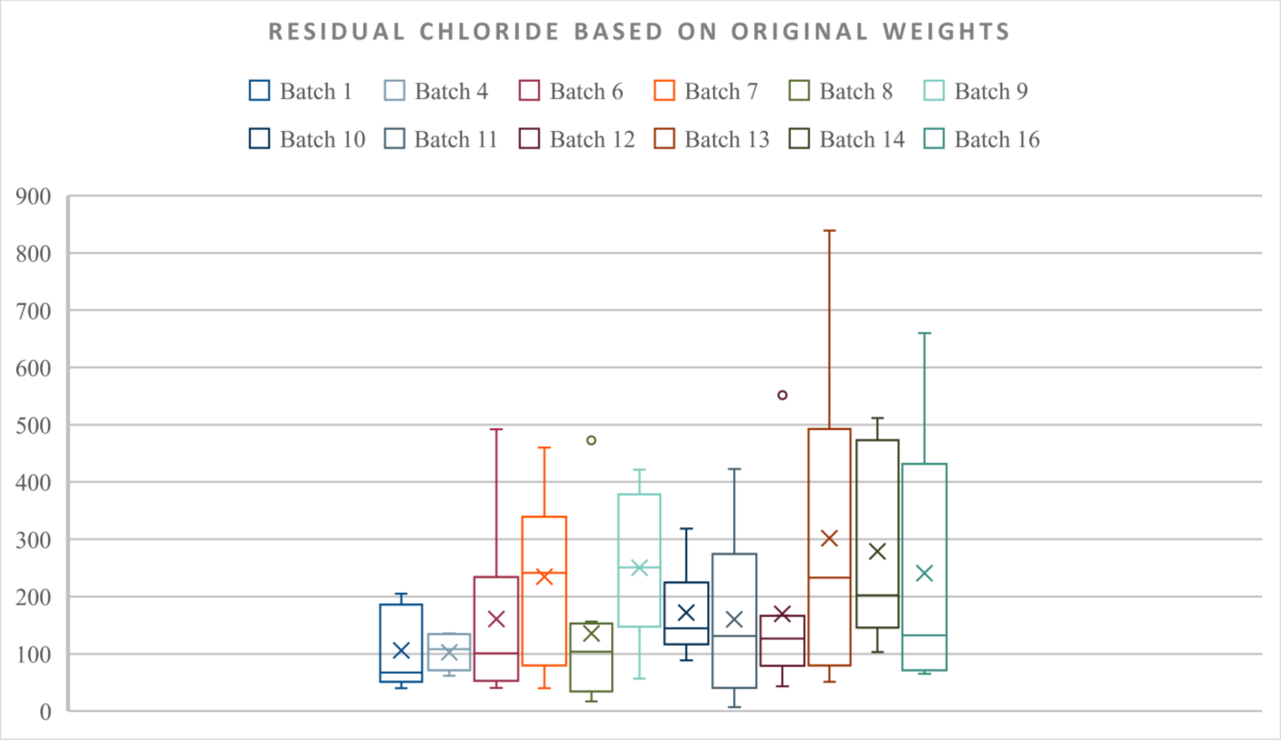
Weker, Wladyslaw Henryk (1989), 'Determination of the concentration of chloride ions extracted from corroded iron artefacts', in Márta Járó (ed.), *International Restorer Seminar* (Veszprém, Hungary: István Éri), 155-56.

Wunderlich, Christian Heinrich (2000), '„Archäosideroprophylakt“ - Entsalzung von Eisenfunden mit Hydroxylamin', *Jahresschrift für mitteldeutsche Vorgeschichte,* 83, 305-16.

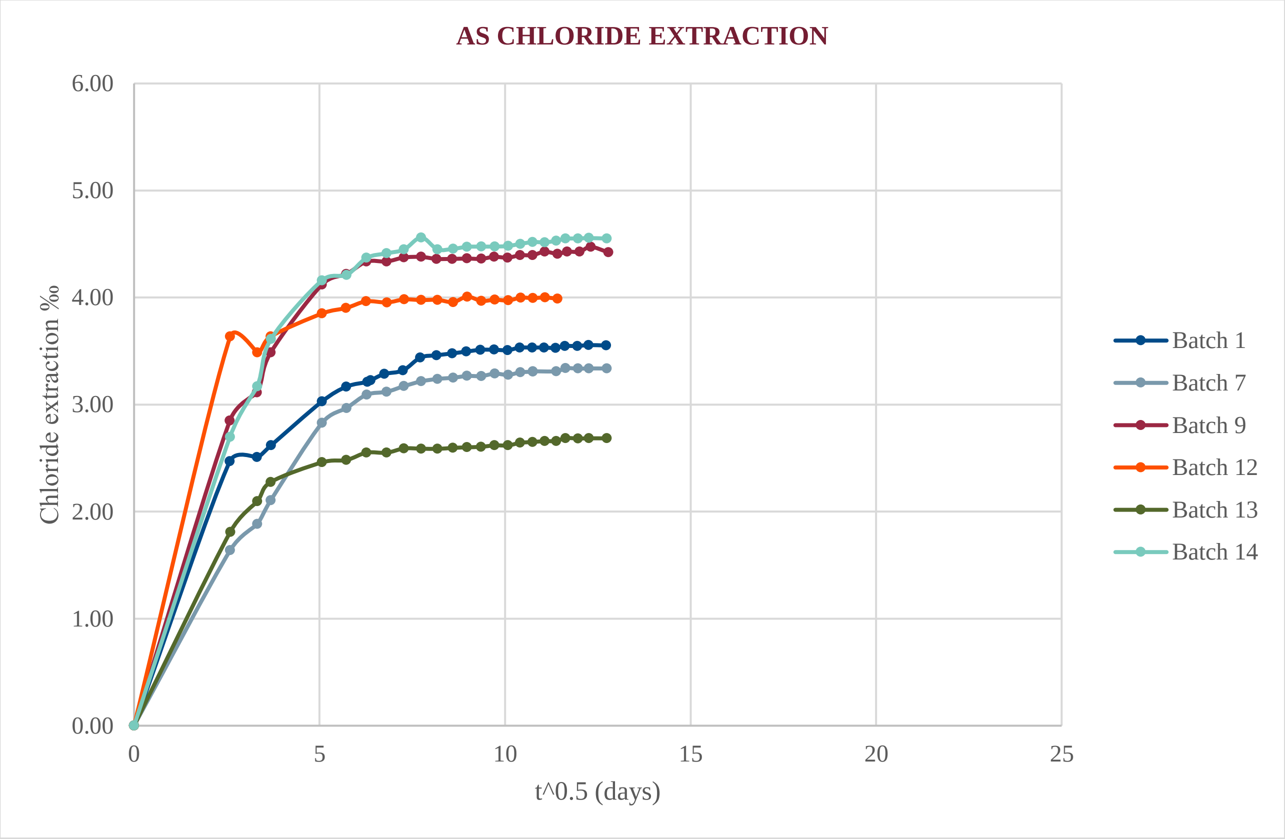
10. Appendices

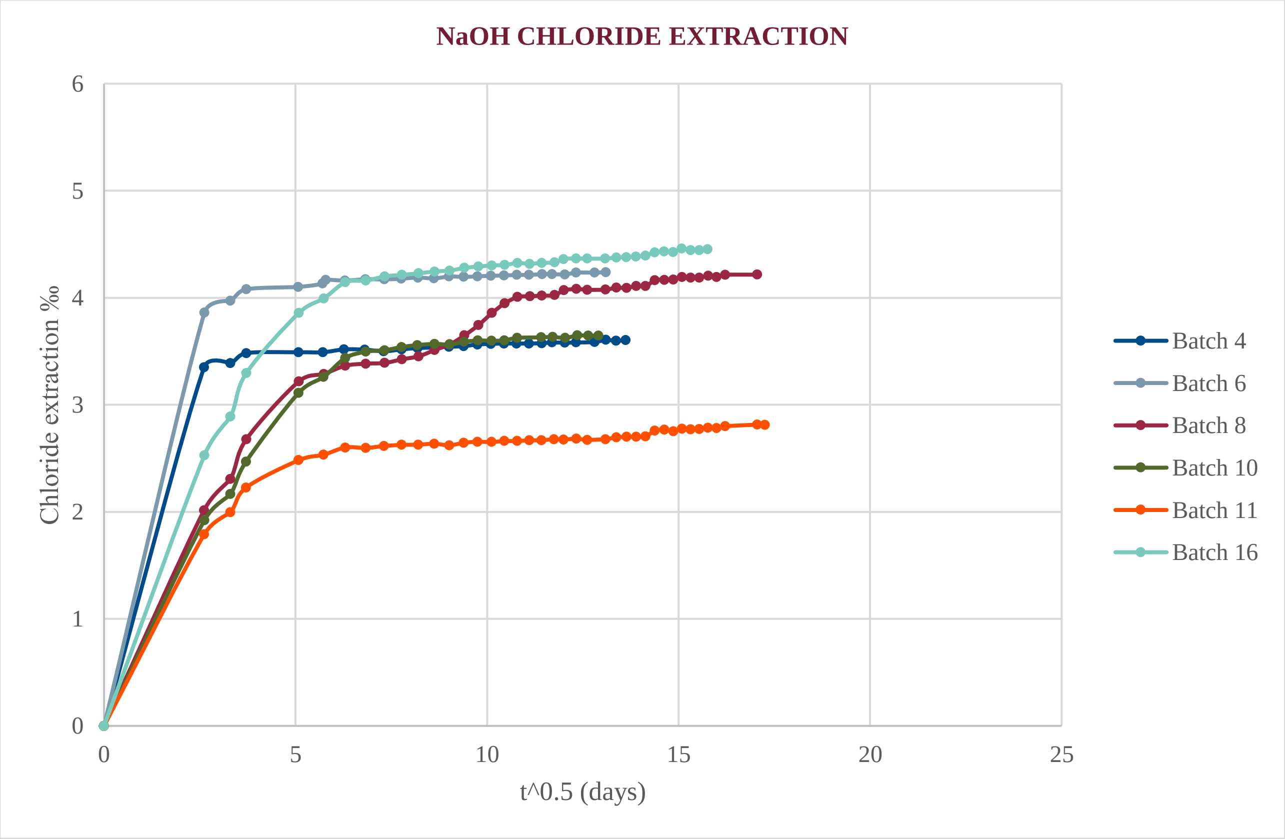
Appendix 1: Residual chloride charts.

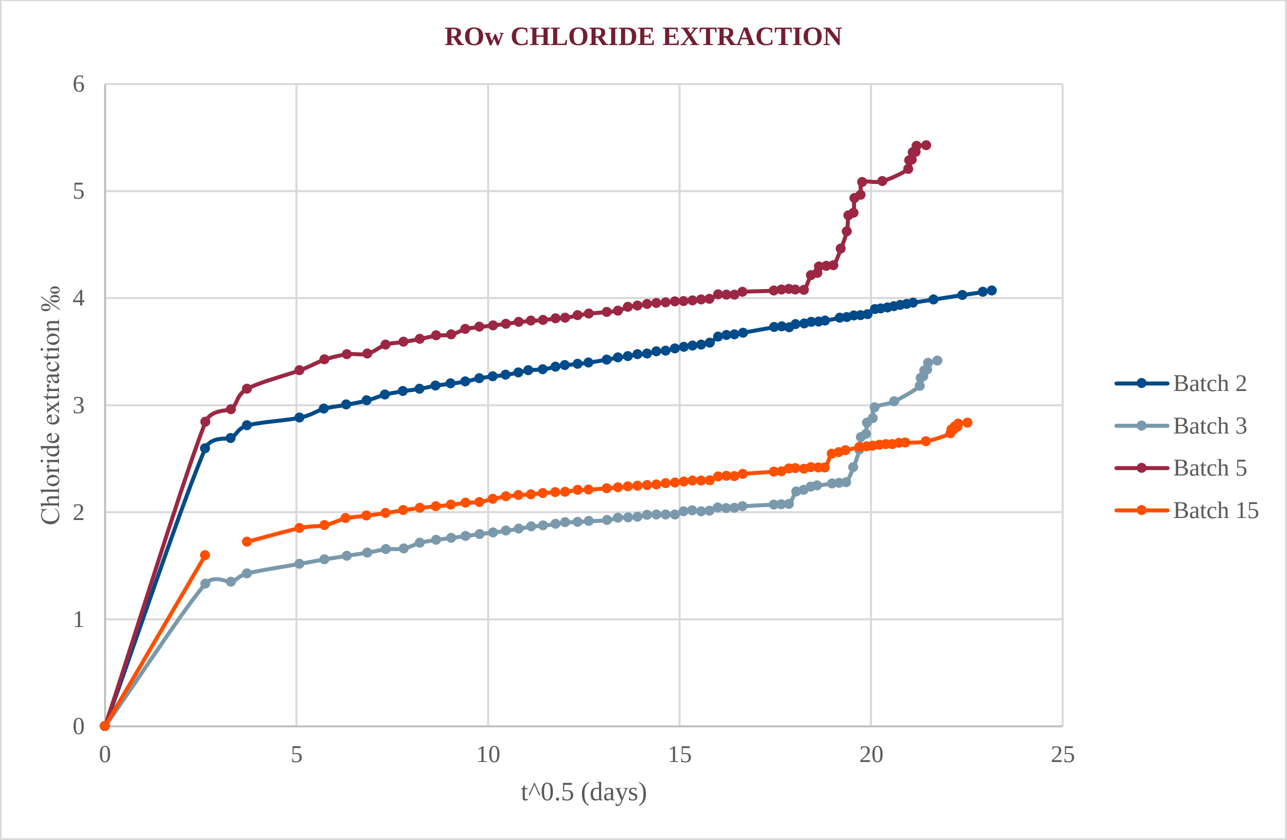




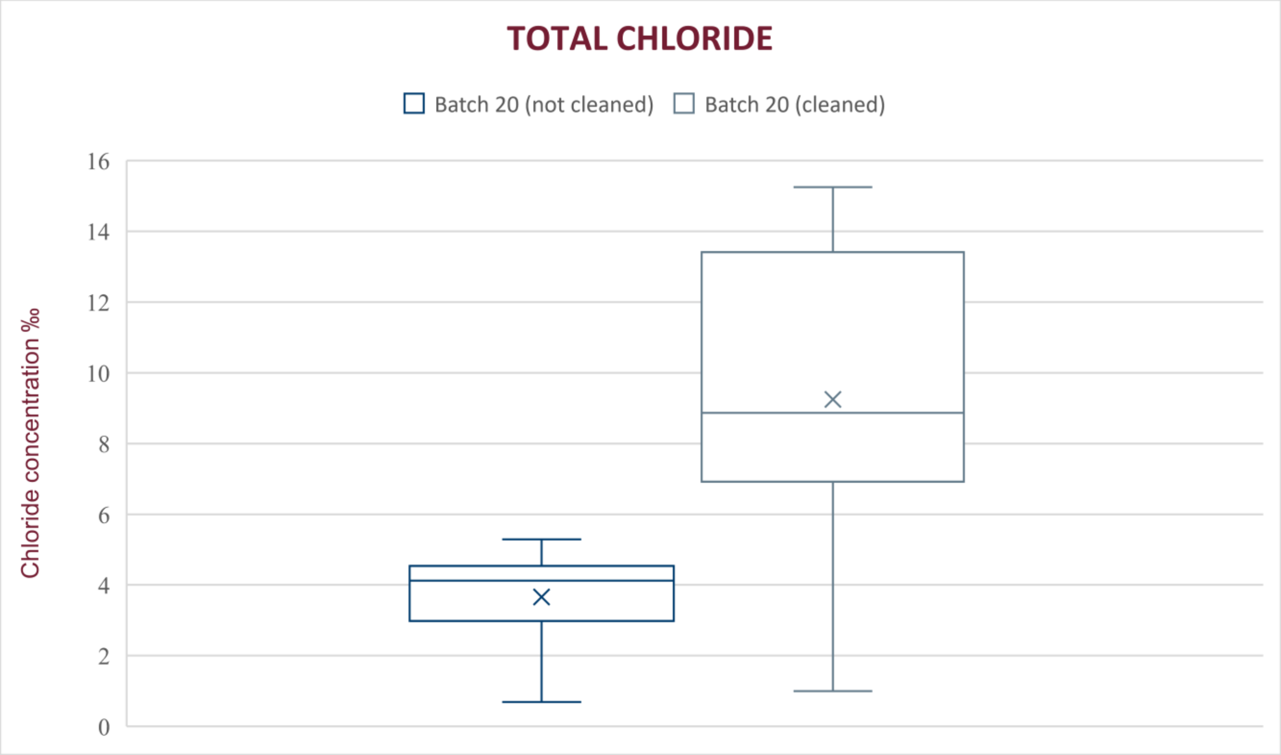
Appendix 2: Chloride extraction charts. Concentrations calculated using uncleaned weights.

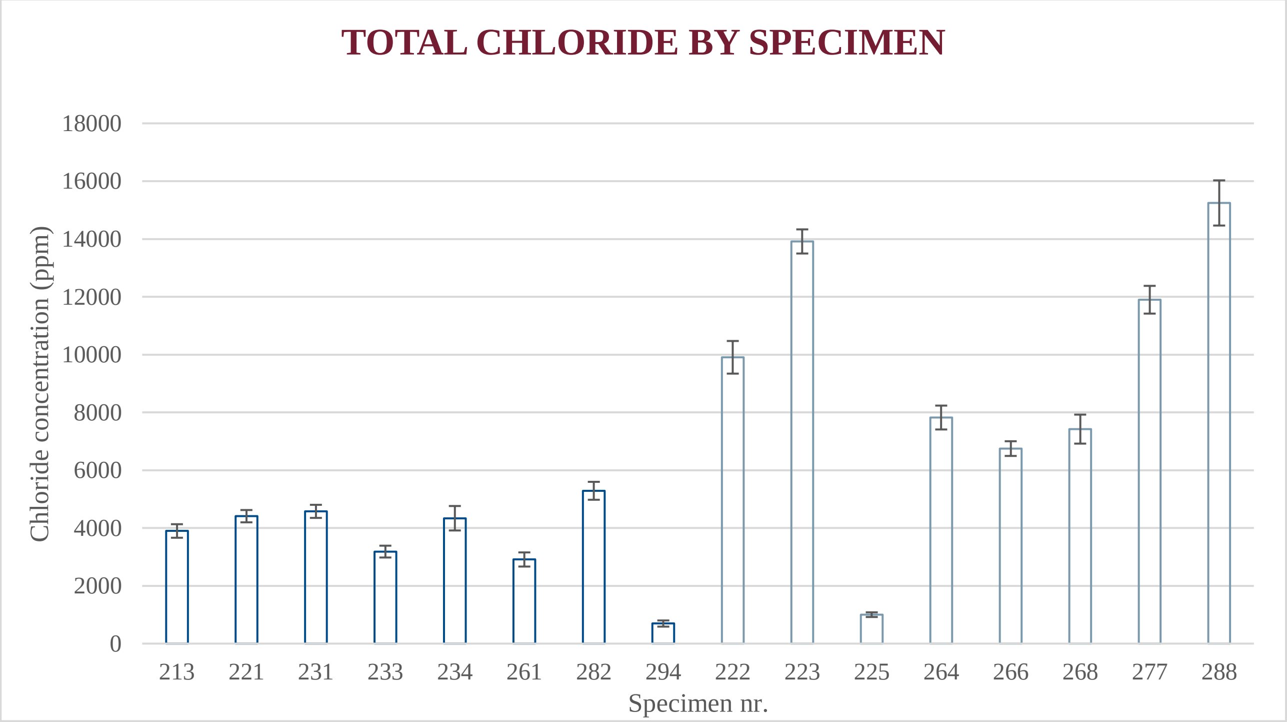




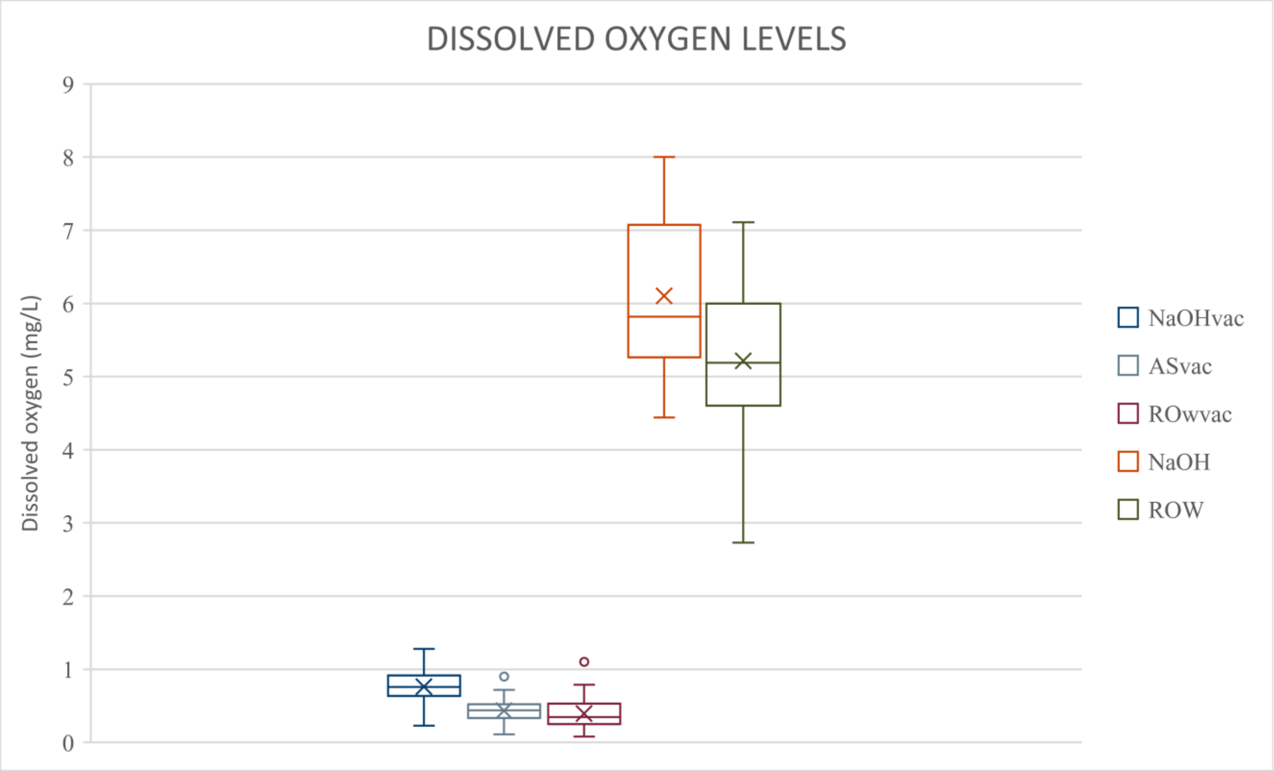

ROw CHLORIDE EXTRACTION
Chloride extraction ‰
0
1
2
3
4
5
6
0
5
10
15
20
25
t^0.5 (days)
Batch 2
Batch 3
Batch 5
Batch 15

Appendix 3: total chloride concentrations. Error as 95 % confidence interval.





Appendix 4: dissolved oxygen levels



Appendix 5: Three-way ANOVA of residual chloride calculated using original weights.

Between-Subjects Factors

		N
Solution type	alk.sulf	47
	NaOH	47
Pressure	ambient	47
	part.vac	47
Cleaning stage	no pre-clean	63
	pre-clean	31

Descriptive Statistics

Dependent Variable: Residualchlorideppm

Solution type	Pressure	Cleaning stage	Mean	Std. Deviation	N
alk.sulf	ambient	no pre-clean	265.821008517641530	216.422517769026170	15
		pre-clean	83.924794445000000	92.308196130852440	8
		Total	202.552760144548840	200.908315931150600	23
	part.vac	no pre-clean	264.643644104441000	142.771234849325030	16
		pre-clean	39.296347916250000	19.089438881732686	8
		Total	189.527878708377360	158.681987604618570	24
	Total	no pre-clean	265.213336562441300	179.025789672961500	31
		pre-clean	61.610571180625000	68.392622022426410	16
		Total	195.901756857993200	178.711765176340700	47
NaOH	ambient	no pre-clean	206.119218298002200	165.527177416807940	16
		pre-clean	82.431920942500000	56.405416605377780	8
		Total	164.890119179501500	149.615732082083130	24
	part.vac	no pre-clean	147.702827342253220	140.995312437418500	16
		pre-clean	48.560765507142854	15.401800910616680	7
		Total	117.529156348958780	125.676739739512980	23

	Total	no pre-clean	176.911022820127670	154.134803458391840	32
		pre-clean	66.625381739333330	44.703288433442230	15
		Total	141.713477794342250	138.993128143476100	47
Total	ambient	no pre-clean	235.007181307505160	190.990854356770200	31
		pre-clean	83.178357693750020	73.903330259957330	16
		Total	183.320773268779960	175.667844252583760	47
	part.vac	no pre-clean	206.173235723347100	151.694811556280230	32
		pre-clean	43.619742792000000	17.514421506273230	15
		Total	154.294461383555500	146.517827390561500	47
	Total	no pre-clean	220.361367677456600	171.368645232849000	63
		pre-clean	64.037092418709690	57.252462500297035	31
		Total	168.807617326167700	161.539168683355370	94

Levene's Test of Equality of Error Variances[a,b]

		Levene Statistic	df1	df2
Residualchlorideppm	Based on Mean	3.805	7	86
	Based on Median	2.792	7	86
	Based on Median and with adjusted df	2.792	7	57.696
	Based on trimmed mean	3.472	7	86

Levene's Test of Equality of Error Variances[a,b]

		Sig.
Residualchlorideppm	Based on Mean	.001
	Based on Median	.011
	Based on Median and with adjusted df	.014
	Based on trimmed mean	.003

Tests the null hypothesis that the error variance of the dependent variable is equal across groups.[a,b]

a. Dependent variable: Residualchlorideppm

b. Design: Intercept + Solutiontype + Pressure + Cleaningstage + Solutiontype * Pressure + Solutiontype * Cleaningstage + Pressure * Cleaningstage + Solutiontype * Pressure * Cleaningstage

Tests of Between-Subjects Effects

Dependent Variable: Residualchlorideppm

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	670255.084[a]	7	95750.726	4.688	<.001
Intercept	1678942.326	1	1678942.326	82.199	<.001
Solutiontype	36938.545	1	36938.545	1.808	.182
Pressure	24701.020	1	24701.020	1.209	.275
Cleaningstage	514222.251	1	514222.251	25.176	<.001
Solutiontype * Pressure	2798.556	1	2798.556	.137	.712
Solutiontype * Cleaningstage	44051.205	1	44051.205	2.157	.146
Pressure * Cleaningstage	462.979	1	462.979	.023	.881
Solutiontype * Pressure * Cleaningstage	5988.804	1	5988.804	.293	.590
Error	1756570.896	86	20425.243		
Total	5105451.077	94			
Corrected Total	2426825.981	93			

Tests of Between-Subjects Effects

Dependent Variable: Residualchlorideppm

Source	Partial Eta Squared
Corrected Model	.276
Intercept	.489
Solutiontype	.021
Pressure	.014
Cleaningstage	.226
Solutiontype * Pressure	.002
Solutiontype * Cleaningstage	.024
Pressure * Cleaningstage	.000
Solutiontype * Pressure * Cleaningstage	.003
Error	
Total	
Corrected Total	

a. R Squared = .276 (Adjusted R Squared = .217)

Estimated Marginal Means

1. Solution type

Dependent Variable: Residualchlorideppm

Solution type	Mean	Std. Error	95% Confidence Interval Lower Bound	Upper Bound
alk.sulf	163.421	22.001	119.685	207.158
NaOH	121.204	22.394	76.685	165.722

2. Pressure

Dependent Variable: Residualchlorideppm

Pressure	Mean	Std. Error	95% Confidence Interval Lower Bound	Upper Bound
ambient	159.574	22.001	115.838	203.310
part.vac	125.051	22.394	80.532	169.570

3. Cleaning stage

Dependent Variable: Residualchlorideppm

Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	Upper Bound
no pre-clean	221.072	18.013	185.263	256.880
pre-clean	63.553	25.712	12.441	114.666

4. Solution type * Pressure

Dependent Variable: Residualchlorideppm

Solution type	Pressure	Mean	Std. Error	95% Confidence Interval Lower Bound	Upper Bound
alk.sulf	ambient	174.873	31.284	112.682	237.064
	part.vac	151.970	30.942	90.459	213.481
NaOH	ambient	144.276	30.942	82.764	205.787
	part.vac	98.132	32.382	33.758	162.506

5. Solution type * Cleaning stage

Dependent Variable: Residualchlorideppm

				95% Confidence Interval	
Solution type	Cleaning stage	Mean	Std. Error	Lower Bound	Upper Bound
alk.sulf	no pre-clean	265.232	25.682	214.178	316.286
	pre-clean	61.611	35.729	-9.417	132.638
NaOH	no pre-clean	176.911	25.264	126.687	227.135
	pre-clean	65.496	36.983	-8.024	139.017

6. Pressure * Cleaning stage

Dependent Variable: Residualchlorideppm

				95% Confidence Interval	
Pressure	Cleaning stage	Mean	Std. Error	Lower Bound	Upper Bound
ambient	no pre-clean	235.970	25.682	184.916	287.024
	pre-clean	83.178	35.729	12.151	154.206
part.vac	no pre-clean	206.173	25.264	155.949	256.397
	pre-clean	43.929	36.983	-29.592	117.449

7. Solution type * Pressure * Cleaning stage

Dependent Variable: Residualchlorideppm

					95% Confidence Interval	
Solution type	Pressure	Cleaning stage	Mean	Std. Error	Lower Bound	Upper Bound
alk.sulf	ambient	no pre-clean	265.821	36.901	192.464	339.178
		pre-clean	83.925	50.529	-16.523	184.373
	part.vac	no pre-clean	264.644	35.729	193.616	335.671
		pre-clean	39.296	50.529	-61.151	139.744
NaOH	ambient	no pre-clean	206.119	35.729	135.092	277.147
		pre-clean	82.432	50.529	-18.016	182.880
	part.vac	no pre-clean	147.703	35.729	76.675	218.730
		pre-clean	48.561	54.018	-58.822	155.944

Appendix 6: Three-way ANOVA of residual chloride calculated using original weights and log-transformed data.

Between-Subjects Factors

		N
Solution type	alk.sulf	47
	NaOH	47
Pressure	ambient	47
	part.vac	47
Cleaning stage	no pre-clean	63
	pre-clean	31

Descriptive Statistics

Dependent Variable: LnResidualchloride

Solution type	Pressure	Cleaning stage	Mean	Std. Deviation	N
alk.sulf	ambient	no pre-clean	5.2256	.94343	15
		pre-clean	4.0363	.89742	8
		Total	4.8119	1.07615	23
	part.vac	no pre-clean	5.4203	.61507	16
		pre-clean	3.5579	.52351	8
		Total	4.7995	1.06511	24
	Total	no pre-clean	5.3261	.78377	31
		pre-clean	3.7971	.75150	16
		Total	4.8056	1.05884	47
NaOH	ambient	no pre-clean	5.0778	.71005	16
		pre-clean	4.2077	.69155	8
		Total	4.7877	.80617	24
	part.vac	no pre-clean	4.4791	1.17569	16
		pre-clean	3.8415	.30858	7
		Total	4.2851	1.02878	23
	Total	no pre-clean	4.7784	1.00263	32
		pre-clean	4.0368	.56185	15
		Total	4.5418	.94639	47
Total	ambient	no pre-clean	5.1493	.82042	31
		pre-clean	4.1220	.77900	16
		Total	4.7996	.93754	47
	part.vac	no pre-clean	4.9497	1.03946	32
		pre-clean	3.6902	.44642	15
		Total	4.5477	1.06816	47
	Total	no pre-clean	5.0479	.93597	63
		pre-clean	3.9131	.66673	31
		Total	4.6737	1.00754	94

Levene's Test of Equality of Error Variances[a,b]

		Levene Statistic	df1	df2	Sig.
LnResidualchloride	Based on Mean	2.676	7	86	.015
	Based on Median	2.031	7	86	.060
	Based on Median and with adjusted df	2.031	7	61.367	.065
	Based on trimmed mean	2.576	7	86	.019

Tests the null hypothesis that the error variance of the dependent variable is equal across groups.[a,b]

a. Dependent variable: LnResidualchloride

b. Design: Intercept + Solutiontype + Pressure + Cleaningstage + Solutiontype * Pressure + Solutiontype * Cleaningstage + Pressure * Cleaningstage + Solutiontype * Pressure * Cleaningstage

Tests of Between-Subjects Effects

Dependent Variable: LnResidualchloride

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	36.502[a]	7	5.215	7.744	<.001
Intercept	1664.382	1	1664.382	2471.860	<.001
Solutiontype	.521	1	.521	.773	.382
Pressure	2.019	1	2.019	2.999	.087
Cleaningstage	26.927	1	26.927	39.991	<.001
Solutiontype * Pressure	.601	1	.601	.892	.347
Solutiontype * Cleaningstage	3.088	1	3.088	4.586	.035
Pressure * Cleaningstage	.251	1	.251	.373	.543
Solutiontype * Pressure * Cleaningstage	1.062	1	1.062	1.578	.213
Error	57.907	86	.673		
Total	2147.658	94			
Corrected Total	94.408	93			

Tests of Between-Subjects Effects

Dependent Variable: LnResidualchloride

Source	Partial Eta Squared
Corrected Model	.387
Intercept	.966
Solutiontype	.009
Pressure	.034
Cleaningstage	.317
Solutiontype * Pressure	.010
Solutiontype * Cleaningstage	.051
Pressure * Cleaningstage	.004
Solutiontype * Pressure * Cleaningstage	.018
Error	
Total	
Corrected Total	

a. R Squared = .387 (Adjusted R Squared = .337)

Estimated Marginal Means

1. Solution type

Dependent Variable: LnResidualchloride

Solution type	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
alk.sulf	4.560	.126	4.309	4.811
NaOH	4.402	.129	4.146	4.657

2. Pressure

Dependent Variable: LnResidualchloride

Pressure	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
ambient	4.637	.126	4.386	4.888
part.vac	4.325	.129	4.069	4.580

3. Cleaning stage

Dependent Variable: LnResidualchloride

Cleaning stage	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
no pre-clean	5.051	.103	4.845	5.256
pre-clean	3.911	.148	3.617	4.204

4. Solution type * Pressure

Dependent Variable: LnResidualchloride

Solution type	Pressure	Mean	Std. Error	95% Confidence Interval	
				Lower Bound	Upper Bound
alk.sulf	ambient	4.631	.180	4.274	4.988
	part.vac	4.489	.178	4.136	4.842
NaOH	ambient	4.643	.178	4.290	4.996
	part.vac	4.160	.186	3.791	4.530

5. Solution type * Cleaning stage

Dependent Variable: LnResidualchloride

Solution type	Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	no pre-clean	5.323	.147	5.030	5.616
	pre-clean	3.797	.205	3.389	4.205
NaOH	no pre-clean	4.778	.145	4.490	5.067
	pre-clean	4.025	.212	3.602	4.447

6. Pressure * Cleaning stage

Dependent Variable: LnResidualchloride

Pressure	Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
ambient	no pre-clean	5.152	.147	4.859	5.445
	pre-clean	4.122	.205	3.714	4.530
part.vac	no pre-clean	4.950	.145	4.661	5.238
	pre-clean	3.700	.212	3.278	4.122

7. Solution type * Pressure * Cleaning stage

Dependent Variable: LnResidualchloride

Solution type	Pressure	Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	ambient	no pre-clean	5.226	.212	4.804	5.647
		pre-clean	4.036	.290	3.460	4.613
	part.vac	no pre-clean	5.420	.205	5.012	5.828
		pre-clean	3.558	.290	2.981	4.135
NaOH	ambient	no pre-clean	5.078	.205	4.670	5.486
		pre-clean	4.208	.290	3.631	4.784
	part.vac	no pre-clean	4.479	.205	4.071	4.887
		pre-clean	3.842	.310	3.225	4.458

Appendix 7: Three-way ANOVA of residual chloride calculated using cleaned weights.

Between-Subjects Factors

		N
Solution type	alk.sulf	47
	NaOH	47
Pressure	ambient	47
	part.vac	47
Cleaning stage	no pre-clean	63
	pre-clean	31

Descriptive Statistics

Dependent Variable: Residualchlorideppm

Solution type	Pressure	Cleaning stage	Mean	Std. Deviation	N
alk.sulf	ambient	no pre-clean	265.821008517641530	216.422517769026170	15
		pre-clean	169.449201245143260	160.182582458817560	8
		Total	232.300379901120380	200.432232736843820	23
	part.vac	no pre-clean	264.643644104441000	142.771234849325030	16
		pre-clean	106.025815067917700	69.552327723233130	8
		Total	211.771034425599940	143.527255940876220	24
	Total	no pre-clean	265.213336562441300	179.025789672961500	31
		pre-clean	137.737508156530500	123.709877202270690	16
		Total	221.817309871067380	172.107100427894660	47
NaOH	ambient	no pre-clean	206.119218298002200	165.527177416807940	16
		pre-clean	160.845930092139670	151.316121454654850	8
		Total	191.028122229381380	159.100221887187500	24
	part.vac	no pre-clean	147.702827342253220	140.995312437418500	16
		pre-clean	102.323156550701140	28.869278118498325	7
		Total	133.891623188302530	119.320757475241220	23

	Total	no pre-clean	176.911022820127670	154.134803458391840	32
		pre-clean	133.535302439468380	112.777575347670490	15
		Total	163.067707805023620	142.475127358643050	47
Total	ambient	no pre-clean	235.007181307505160	190.990854356770200	31
		pre-clean	165.147565668641480	150.594657595573120	16
		Total	211.225184494274900	179.734701394933670	47
	part.vac	no pre-clean	206.173235723347100	151.694811556280230	32
		pre-clean	104.297907759883330	52.721964900943085	15
		Total	173.659833181816140	136.593597717131200	47
	Total	no pre-clean	220.361367677456600	171.368645232849000	63
		pre-clean	135.704182809564940	116.584970157902260	31
		Total	192.442508838045500	159.886766144658620	94

Levene's Test of Equality of Error Variances[a,b]

		Levene Statistic	df1	df2
Residualchlorideppm	Based on Mean	1.686	7	86
	Based on Median	1.277	7	86
	Based on Median and with adjusted df	1.277	7	67.803
	Based on trimmed mean	1.541	7	86

Levene's Test of Equality of Error Variances[a,b]

		Sig.
Residualchlorideppm	Based on Mean	.123
	Based on Median	.271
	Based on Median and with adjusted df	.275
	Based on trimmed mean	.164

Tests the null hypothesis that the error variance of the dependent variable is equal across groups.[a,b]

a. Dependent variable: Residualchlorideppm

b. Design: Intercept + Solutiontype + Pressure + Cleaningstage + Solutiontype * Pressure + Solutiontype * Cleaningstage + Pressure * Cleaningstage + Solutiontype * Pressure * Cleaningstage

Tests of Between-Subjects Effects

Dependent Variable: Residualchlorideppm

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	328002.721[a]	7	46857.532	1.966	.069
Intercept	2622629.043	1	2622629.043	110.053	<.001
Solutiontype	46244.104	1	46244.104	1.941	.167
Pressure	42688.762	1	42688.762	1.791	.184
Cleaningstage	154747.564	1	154747.564	6.494	.013
Solutiontype * Pressure	3548.219	1	3548.219	.149	.701
Solutiontype * Cleaningstage	34981.490	1	34981.490	1.468	.229
Pressure * Cleaningstage	5035.884	1	5035.884	.211	.647
Solutiontype * Pressure * Cleaningstage	5001.575	1	5001.575	.210	.648
Error	2049428.632	86	23830.565		
Total	5858638.558	94			
Corrected Total	2377431.353	93			

Tests of Between-Subjects Effects

Dependent Variable: Residualchlorideppm

Source	Partial Eta Squared
Corrected Model	.138
Intercept	.561
Solutiontype	.022
Pressure	.020
Cleaningstage	.070
Solutiontype * Pressure	.002
Solutiontype * Cleaningstage	.017
Pressure * Cleaningstage	.002
Solutiontype * Pressure * Cleaningstage	.002
Error	
Total	
Corrected Total	

a. R Squared = .138 (Adjusted R Squared = .068)

Estimated Marginal Means

1. Solution type

Dependent Variable: Residualchlorideppm

Solution type	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	201.485	23.764	154.243	248.726
NaOH	154.248	24.189	106.161	202.335

2. Pressure

Dependent Variable: Residualchlorideppm

Pressure	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
ambient	200.559	23.764	153.317	247.800
part.vac	155.174	24.189	107.087	203.261

3. Cleaning stage

Dependent Variable: Residualchlorideppm

Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
no pre-clean	221.072	19.457	182.393	259.750
pre-clean	134.661	27.772	79.451	189.871

4. Solution type * Pressure

Dependent Variable: Residualchlorideppm

Solution type	Pressure	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	ambient	217.635	33.792	150.459	284.811
	part.vac	185.335	33.422	118.893	251.776
NaOH	ambient	183.483	33.422	117.041	249.924
	part.vac	125.013	34.978	55.479	194.546

5. Solution type * Cleaning stage

Dependent Variable: Residualchlorideppm

Solution type	Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	no pre-clean	265.232	27.740	210.086	320.378
	pre-clean	137.738	38.593	61.017	214.458
NaOH	no pre-clean	176.911	27.289	122.662	231.160
	pre-clean	131.585	39.947	52.172	210.997

6. Pressure * Cleaning stage

Dependent Variable: Residualchlorideppm

Pressure	Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
ambient	no pre-clean	235.970	27.740	180.824	291.116
	pre-clean	165.148	38.593	88.427	241.868
part.vac	no pre-clean	206.173	27.289	151.924	260.423
	pre-clean	104.174	39.947	24.762	183.587

7. Solution type * Pressure * Cleaning stage

Dependent Variable: Residualchlorideppm

Solution type	Pressure	Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	ambient	no pre-clean	265.821	39.859	186.585	345.057
		pre-clean	169.449	54.579	60.951	277.948
	part.vac	no pre-clean	264.644	38.593	187.924	341.364
		pre-clean	106.026	54.579	-2.473	214.524
NaOH	ambient	no pre-clean	206.119	38.593	129.399	282.839
		pre-clean	160.846	54.579	52.347	269.345
	part.vac	no pre-clean	147.703	38.593	70.983	224.423
		pre-clean	102.323	58.347	-13.667	218.313

Appendix 8: Three-way ANOVA of residual chloride calculated using cleaned weights and log transformed data.

Between-Subjects Factors

		N
Solution type	alk.sulf	47
	NaOH	47
Pressure	ambient	47
	part.vac	47
Cleaning stage	no pre-clean	63
	pre-clean	31

Descriptive Statistics

Dependent Variable: lnresidualchloride

Solution type	Pressure	Cleaning stage	Mean	Std. Deviation	N
alk.sulf	ambient	no pre-clean	5.2256	.94343	15
		pre-clean	4.8612	.74261	8
		Total	5.0988	.87941	23
	part.vac	no pre-clean	5.4203	.61507	16
		pre-clean	4.4727	.65770	8
		Total	5.1044	.76588	24
	Total	no pre-clean	5.3261	.78377	31
		pre-clean	4.6669	.70672	16
		Total	5.1017	.81435	47
NaOH	ambient	no pre-clean	5.0778	.71005	16
		pre-clean	4.7467	.86055	8
		Total	4.9674	.76132	24
	part.vac	no pre-clean	4.4791	1.17569	16
		pre-clean	4.5906	.30362	7
		Total	4.5130	.98505	23
	Total	no pre-clean	4.7784	1.00263	32
		pre-clean	4.6738	.64520	15
		Total	4.7451	.89810	47
Total	ambient	no pre-clean	5.1493	.82042	31
		pre-clean	4.8039	.77874	16
		Total	5.0317	.81492	47
	part.vac	no pre-clean	4.9497	1.03946	32
		pre-clean	4.5277	.50941	15
		Total	4.8150	.92014	47
	Total	no pre-clean	5.0479	.93597	63
		pre-clean	4.6703	.66633	31
		Total	4.9234	.87127	94

Levene's Test of Equality of Error Variances[a,b]

		Levene Statistic	df1	df2	Sig.
lnresidualchloride	Based on Mean	2.333	7	86	.031
	Based on Median	1.844	7	86	.089
	Based on Median and with adjusted df	1.844	7	66.689	.093
	Based on trimmed mean	2.255	7	86	.037

Tests the null hypothesis that the error variance of the dependent variable is equal across groups.[a,b]

a. Dependent variable: lnresidualchloride

b. Design: Intercept + Solutiontype + Pressure + Cleaningstage + Solutiontype * Pressure + Solutiontype * Cleaningstage + Pressure * Cleaningstage + Solutiontype * Pressure * Cleaningstage

Tests of Between-Subjects Effects

Dependent Variable: lnresidualchloride

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	11.541[a]	7	1.649	2.401	.027
Intercept	1957.425	1	1957.425	2850.444	<.001
Solutiontype	1.527	1	1.527	2.223	.140
Pressure	1.165	1	1.165	1.697	.196
Cleaningstage	3.039	1	3.039	4.425	.038
Solutiontype * Pressure	.408	1	.408	.594	.443
Solutiontype * Cleaningstage	1.545	1	1.545	2.251	.137
Pressure * Cleaningstage	.026	1	.026	.037	.847
Solutiontype * Pressure * Cleaningstage	1.363	1	1.363	1.984	.163
Error	59.057	86	.687		
Total	2349.121	94			
Corrected Total	70.598	93			

Tests of Between-Subjects Effects

Dependent Variable: lnresidualchloride

Source	Partial Eta Squared
Corrected Model	.163
Intercept	.971
Solutiontype	.025
Pressure	.019
Cleaningstage	.049
Solutiontype * Pressure	.007
Solutiontype * Cleaningstage	.026
Pressure * Cleaningstage	.000
Solutiontype * Pressure * Cleaningstage	.023
Error	
Total	
Corrected Total	

a. R Squared = .163 (Adjusted R Squared = .095)

Estimated Marginal Means

1. Solution type

Dependent Variable: lnresidualchloride

Solution type	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	4.995	.128	4.741	5.249
NaOH	4.724	.130	4.465	4.982

2. Pressure

Dependent Variable: lnresidualchloride

Pressure	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
ambient	4.978	.128	4.724	5.231
part.vac	4.741	.130	4.483	4.999

3. Cleaning stage

Dependent Variable: lnresidualchloride

Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
no pre-clean	5.051	.104	4.843	5.258
pre-clean	4.668	.149	4.371	4.964

4. Solution type * Pressure

Dependent Variable: lnresidualchloride

Solution type	Pressure	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	ambient	5.043	.181	4.683	5.404
	part.vac	4.947	.179	4.590	5.303
NaOH	ambient	4.912	.179	4.556	5.269
	part.vac	4.535	.188	4.162	4.908

5. Solution type * Cleaning stage

Dependent Variable: lnresidualchloride

Solution type	Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	no pre-clean	5.323	.149	5.027	5.619
	pre-clean	4.667	.207	4.255	5.079
NaOH	no pre-clean	4.778	.146	4.487	5.070
	pre-clean	4.669	.214	4.242	5.095

6. Pressure * Cleaning stage

Dependent Variable: lnresidualchloride

Pressure	Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
ambient	no pre-clean	5.152	.149	4.856	5.448
	pre-clean	4.804	.207	4.392	5.216
part.vac	no pre-clean	4.950	.146	4.658	5.241
	pre-clean	4.532	.214	4.105	4.958

7. Solution type * Pressure * Cleaning stage

Dependent Variable: lnresidualchloride

Solution type	Pressure	Cleaning stage	Mean	Std. Error	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
alk.sulf	ambient	no pre-clean	5.226	.214	4.800	5.651
		pre-clean	4.861	.293	4.279	5.444
	part.vac	no pre-clean	5.420	.207	5.008	5.832
		pre-clean	4.473	.293	3.890	5.055
NaOH	ambient	no pre-clean	5.078	.207	4.666	5.490
		pre-clean	4.747	.293	4.164	5.329
	part.vac	no pre-clean	4.479	.207	4.067	4.891
		pre-clean	4.591	.313	3.968	5.213

Appendix 9: Three-way ANOVA of deterioration:

Between-Subjects Factors

		Value Label	N
Solution type	1	NaOH	41
	2	AS	48
	3	ROw	26
Pressure	1	amb	56
	2	vac	59
Cleaning stage	1	Pre-cleaning	38
	2	No pre-cleaning	77

Descriptive Statistics

Dependent Variable: Change in integrity

Solution type	Pressure	Cleaning stage	Mean	Std. Deviation	N
NaOH	amb	Pre-cleaning	-.83	.983	6
		No pre-cleaning	-.43	.852	14
		Total	-.55	.887	20
	vac	Pre-cleaning	-.80	.837	5
		No pre-cleaning	-.69	.946	16
		Total	-.71	.902	21
	Total	Pre-cleaning	-.82	.874	11
		No pre-cleaning	-.57	.898	30
		Total	-.63	.888	41
AS	amb	Pre-cleaning	-1.62	1.302	8
		No pre-cleaning	-1.19	1.167	16
		Total	-1.33	1.204	24
	vac	Pre-cleaning	-1.12	1.356	8
		No pre-cleaning	-.75	.775	16
		Total	-.87	.992	24
	Total	Pre-cleaning	-1.38	1.310	16
		No pre-cleaning	-.97	.999	32
		Total	-1.10	1.115	48
ROw	amb	Pre-cleaning	-1.80	1.304	5
		No pre-cleaning	.00	.000	7
		Total	-.75	1.215	12
	vac	Pre-cleaning	-.83	1.169	6

		No pre-cleaning	-.25	.463	8
		Total	-.50	.855	14
	Total	Pre-cleaning	-1.27	1.272	11
		No pre-cleaning	-.13	.352	15
		Total	-.62	1.023	26
Total	amb	Pre-cleaning	-1.42	1.216	19
		No pre-cleaning	-.68	1.029	37
		Total	-.93	1.142	56
	vac	Pre-cleaning	-.95	1.129	19
		No pre-cleaning	-.62	.807	40
		Total	-.73	.925	59
	Total	Pre-cleaning	-1.18	1.182	38
		No pre-cleaning	-.65	.914	77
		Total	-.83	1.037	115

Levene's Test of Equality of Error Variances[a,b]

		Levene Statistic	df1	df2	Sig.
Change in integrity	Based on Mean	2.995	11	103	.002
	Based on Median	1.585	11	103	.114
	Based on Median and with adjusted df	1.585	11	79.539	.119
	Based on trimmed mean	2.839	11	103	.003

Tests the null hypothesis that the error variance of the dependent variable is equal across groups.[a,b]

a. Dependent variable: Change in integrity

b. Design: Intercept + Solutiontype + Pressure + Cleaningstage + Solutiontype * Pressure + Solutiontype * Cleaningstage + Pressure * Cleaningstage + Solutiontype * Pressure * Cleaningstage

Tests of Between-Subjects Effects

Dependent Variable: Change in integrity

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	22.702[a]	11	2.064	2.130	.024
Intercept	70.529	1	70.529	72.776	<.001
Solutiontype	5.408	2	2.704	2.790	.066
Pressure	1.351	1	1.351	1.394	.240
Cleaningstage	9.130	1	9.130	9.421	.003
Solutiontype * Pressure	1.636	2	.818	.844	.433
Solutiontype * Cleaningstage	3.493	2	1.746	1.802	.170
Pressure * Cleaningstage	1.635	1	1.635	1.687	.197
Solutiontype * Pressure * Cleaningstage	1.373	2	.687	.709	.495
Error	99.820	103	.969		
Total	201.000	115			
Corrected Total	122.522	114			

Tests of Between-Subjects Effects

Dependent Variable: Change in integrity

Source	Partial Eta Squared
Corrected Model	.185
Intercept	.414
Solutiontype	.051
Pressure	.013
Cleaningstage	.084
Solutiontype * Pressure	.016
Solutiontype * Cleaningstage	.034
Pressure * Cleaningstage	.016
Solutiontype * Pressure * Cleaningstage	.014
Error	
Total	
Corrected Total	

a. R Squared = .185 (Adjusted R Squared = .098)

Post Hoc Tests

Solution type

Multiple Comparisons

Dependent Variable: Change in integrity
Tukey HSD

(I) Solution type	(J) Solution type	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval Lower Bound	95% Confidence Interval Upper Bound
NaOH	AS	.47	.209	.068	-.03	.97
	ROw	-.02	.247	.997	-.61	.57
AS	NaOH	-.47	.209	.068	-.97	.03
	ROw	-.49	.240	.108	-1.06	.08
ROw	NaOH	.02	.247	.997	-.57	.61
	AS	.49	.240	.108	-.08	1.06

Based on observed means.
The error term is Mean Square(Error) = .969.

Homogeneous Subsets

Change in integrity

Tukey HSD[a,b,c]

Solution type	N	Subset 1
AS	48	-1.10
NaOH	41	-.63
ROw	26	-.62
Sig.		.094

Means for groups in homogeneous subsets are displayed.
Based on observed means.
The error term is Mean Square(Error) = .969.

a. Uses Harmonic Mean Sample Size = 35.849.

b. The group sizes are unequal. The harmonic mean of the group sizes is used. Type I error levels are not guaranteed.

c. Alpha = .05.