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Extended Abstracts

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Extended Abstracts

Session 4

Marine Finds

EFFECT OF DECHLORINATION IN NaOH OF IRON ARCHAEOLOGICAL ARTEFACTS IMMERSED IN SEA WATER

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Introduction

The aim of the dechlorination treatments is to remove the chloride and the Cl-containing phases present inside the corrosion layers. Dechlorination of iron artefacts has been widely studied in order to understand the physico-chemical mechanisms involved. The final goal is to optimise the various dechlorination treatments tested by the conservation laboratories. A general tendency to agree on the fact that dechlorination is more efficient on artefacts freshly excavated stands in the literature (Drews et al. 2004). Treating an artefact after excavation stops or reduces the corrosion phenomena. The consequence is a limitation of the activation of the corrosion processes when artefact is exposed to air through the migration of chloride ions inside the corrosion layers. The precipitation of akaganeite (β-FeOOH) is often associated to these phenomenons (Selwyn 2004) specifically on the artefacts stored during long periods.

Our methodology initiated by the Odefa project was to characterise the evolution at a microscopic scale of the corrosion layers during a dechlorination treatment consisting in soaking of the artefacts in NaOH 2%. Treatments in basic solutions are the most common in conservation workshop. Artefacts excavated from the marine site of Les Saintes Maries de la Mer were chosen to establish the set of samples. Some of them were freshly excavated while others were excavated and stored without any protection against air two years before applying the treatment. In a first time the entire ingots were treated and transverse sections were analysed.

Two complementary analytical protocols have been followed. The first one is based on the treatment of entire iron ingots in basic medium with or without cathodic polarisation. Transverse sections of the treated ingots were afterwards analysed. The second consists in characterising the structural evolution of the phases in situ in solution during the treatment. For this last protocol the treatment in soda 2%wt has been given priority. Characterisation of the corrosion products on transverse sections were based on a combination of microbeam analytical tools: µraman spectroscopy (532 nm, Ø 2 µm), X-ray microdiffraction (µXRD, 17 keV and 30x600 µm²) and Energy Dispersive Spectroscopy coupled to Scanning Electron Microscope).

Before treatment

The observations highlighted by the Odefa project are briefly reminded in this paragraph. One freshly excavated ingot stored only nine weeks in tap water has been analysed. Corrosion products of several millimetres thickness were present and a concretion layer (mainly calcite or quartz) was partly present on the external surface. The inner part of the corrosion layer was mainly composed of an iron hydroxychloride (β-Fe$_2$(OH)$_3$Cl). On the external part a thin layer of magnetite (few 10 µm thickness) almost continuous has been observed. Its presence has been attributed to the first stage of corrosion. Between the β -Fe$_2$(OH)$_3$Cl and the magnetite layer a thin layer of akaganeite (few 10 µm thickness) was also observed. Its presence could be explained by a weak release of chloride during the storage of the ingot in aerated tap water. This process provoked an oxidation of the superficial part of the β-Fe$_2$(OH)$_3$Cl and induced the precipitation of akaganeite on the ingot during the immersion in the tap water or during the drying of the ingot when it was prepared for the analyses. The average Cl content of the layer is about 18%wt. The corrosion layers of the ingot stored during two years at ambient RH and temperature were completely different. The corrosion products were mainly composed of iron oxy-hydroxides. Goethite (α-FeOOH) was the main constituent but akaganeite (β-FeOOH) was present in veins more or less parallel to metal/corrosion product interface. Moreover marbles were observed by optical microscope and were correlated to less crystallised phases as feroxyxhyte (δ-FeOOH)/ferrihydrite (5Fe$_2$O$_3$, 9H$_2$O). The average Cl content of the layer is about 4%wt.

After treatment on entire ingots

Cathodic polarisation in KOH 1%wt and soaking in NaOH 2%wt have been applied on fresh and stored ingots. On the freshly excavated ingots chlorides extracted from the Cl containing phases were not detected anymore. The corrosion products have evolved towards a system composed of goethite and less crystallised ferrihydrite and/or feroxyhyte. Moreover a layer of magnetite has been detected at the metal/corrosion product interface. On the two-year stored ingots goethite and ferrihydrite and/or feroxyhyte were present in the layer but akaganeite is not completely removed from the external part of the corrosion layer.

In situ dechlorination

To determine how the crystalline phases transform inside the corrosion layer during a treatment and identify the intermediate phases formed in solution, partial treatment in 2%wt NaOH on samples cut on a freshly excavated ingot have been conducted. Sample was put in a cell so that μXRD could be performed on the transverse section allowing the transformation of the phases inside the corrosion layer to be followed. The samples were carefully selected in order to present both akaganeite and β-$Fe_2(OH)_3Cl$ allowing to compare the behaviour of both phases in the same conditions. Firstly it has been noticed that akaganeite contrary to β-$Fe_2(OH)_3Cl$ could not be dechlorinated during treatment lasting at the most 35h. Secondly after 8h of treatment the dechlorination front is located at about 600 μm of the surface in the β-$Fe_2(OH)_3Cl$ zone. Magnetite has been mainly observed in situ in the dechlorinated zone but $Fe(OH)_2$ was also detected during the dechlorination process. Observations have been completed using raman microspectroscopy of the sample after the interruption of the treatment. On the dried sample the dechlorinated zone is composed of a mix of goethite and magnetite and the dechlorination front have been correlated to the presence of akaganeite, goethite, magnetite and ferrihydrite. The presence of akaganeite on the dried sample and not in situ could be explained by the interruption of the treatment that induced its precipitation. Last in the not dechlorinated zones the β-$Fe_2(OH)_3Cl$ was still the main phase detected by raman spectroscopy but some akaganeite was also present under the dechlorination front in the corrosion layer.

Dechlorination mechanisms

The *E*-pH equilibrium Pourbaix diagram of iron in concentrated chloride aqueous solution was recently established (Remazeilles et al. 2009). It shows that an equilibrium exists between the two ferrous phases β-$Fe_2(OH)_3Cl$ and $Fe(OH)_2$. This equilibrium is more favourable for $Fe(OH)_2$ under alkaline conditions. In consequence, immersing objects containing β-$Fe_2(OH)_3Cl$ in the rust layer leads to the release of chlorides, according to the chemical reaction:

$$\beta\text{-}Fe_2(OH)_3Cl + OH^- \rightarrow 2\ Fe(OH)_2 + Cl^-$$

$Fe(OH)_2$ was detected in situ in the reactor. Magnetite was also detected and may result from the oxidation of $Fe(OH)_2$.

Consequences for conservation

The dechlorination rate of β-$Fe_2(OH)_3Cl$ in alkaline media proved to be higher than that of akaganéite. So, for artefacts that remained in anoxic conditions, the dechlorination was more efficient for freshly excavated objects. In this case, the rust layer more likely contained only β-$Fe_2(OH)_3Cl$, even if a small amount of akaganéite could have been present as the result of a slight oxidation of the β-$Fe_2(OH)_3Cl$ layer.

Finally, when $Fe(OH)_2$ forms from $\beta\text{-}Fe_2(OH)_3Cl$, the next steps of the treatment will have an influence on the final corrosion products because this phase is very reactive towards O_2. A step favouring a slow oxidation process of $Fe(OH)_2$ (long treatment, soft drying) should lead to the formation of magnetite (and possibly goethite), while a step favouring a fast oxidation process (rinsing in ethanol for instance) should lead to poorly crystallized phases such as $\delta\text{-}FeOOH$.

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EVOLUTION OF pH IN THE SOLUTIONS OF DECHLORINATION

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Introduction

Archaeological iron artefacts are usually stabilized by electrolysis or by immersion in alkaline sulphite. For the two treatments, measurements of the chloride concentration are taken every week by argentimetry – potentiometry. The treatment solution is changed when the chloride concentration "stops" increasing. In Arc'Antique, the monitoring of the dechlorination treatment also includes the pH measurement over 2 years. For the electrolysis, the solution of KOH (1%w) initially has a pH of 13.3. The pH decreases during the treatment. The value is approximately 10.5 at the end of each bath. These evolutions of the pH seem to be correlated with those of chloride concentrations. When the chloride concentration stops increasing, the pH decreases. For the dechlorination by immersion in alkaline sulphite, with the high concentrations (NaOH 0.5M + Na_2SO_3 0.5M), the pH of the solution remains at 13.5 during all the treatment. But if we use the lower concentrations ((NaOH 0.1M + Na_2SO_3 0.05M) concentration advised in the Wang's paper), the pH decreases during the treatment and it can reach a value of 10 at the end of the bath. In this presentation, we'll try correlating the evolution of the pH with the impacts of dechlorination.

The dechlorination of iron artefacts

The ferrous archaeological artefacts contain chlorinated corrosion products. After excavation, the chloride corrosion cycle can provoke the rapid destruction of the archaeological object. For this reason, the objects are currently treated to remove chloride ions. Desalination methods have been employed for several decades in order to stabilize iron archaeological artefacts. Electrochemical and immersion treatments are currently used. In literature (North 1978, North 1987, Mardikian 2005, Selwyn 2001), it is mentioned that the immersion methods extract the chloride by diffusion; and the electrolysis favours the extraction of chlorides by reducing the CPs. In the electrolysis, the electric field applied to the iron artefacts also accelerates the chloride removal. The solution of the desalination treatments is chosen so that the artefact remains in the passive zone of the Pourbaix diagram, it's an alkaline solution. For the electrolysis, the objects are polarized at -1.45V/SSE (or -0.8V/NHE) with a stabilised generator in an alkaline solution (as KOH 1%) maintained at room temperature and stirred every week. For the immersion in the alkaline sulphite, the objects are immersed in a closed tank, and the solution is regularly stirred and heated (50°C). The alkaline sulphite solution is made of soda (NaOH, 0.5M) and sodium sulphite (Na_2SO_3, 0.5M) (North 1978), but in a

recent paper (Wang 2008), the treatments are also effective in less concentrated solutions (0.1M NaOH and 0.05M Na$_2$SO$_3$).

During the stabilisation treatments, the main parameters of the treatment solution (temperature, pH and chloride content) were monitored for this paper. The chloride content was quantified using argentimetry / potentiometry and the pH was measured by a glass electrode (with corrections of the temperature).

Results and discussion

Electrolysis

During the treatments of the archaeological artefacts, only the chloride rate was measured. But since a research program on the comparison of the iron stabilization, several parameters have been monitored: chloride rate, pH, temperature, conductivity. For this study, a Roman iron ingot (from *"Saintes Maries de la Mer"*, near Marseille in France) was treated by electrolysis in 10L of KOH (1% (w/w)). The results of pH and chloride rate are showed in Fig. 1. We notice the decrease of pH from 13 to 10.5 in each bath. In the first bath, the pH has remained to 13 for 3 days, whereas it has remained to 13 for 8 days in the third bath. The evolution of pH wouldn't depend on time but on the evolution of the chloride rate. The pH decreases when the chloride rate increases, and the pH stabilizes at 10.5 when the chloride rate reaches its maximum value (whatever the value).
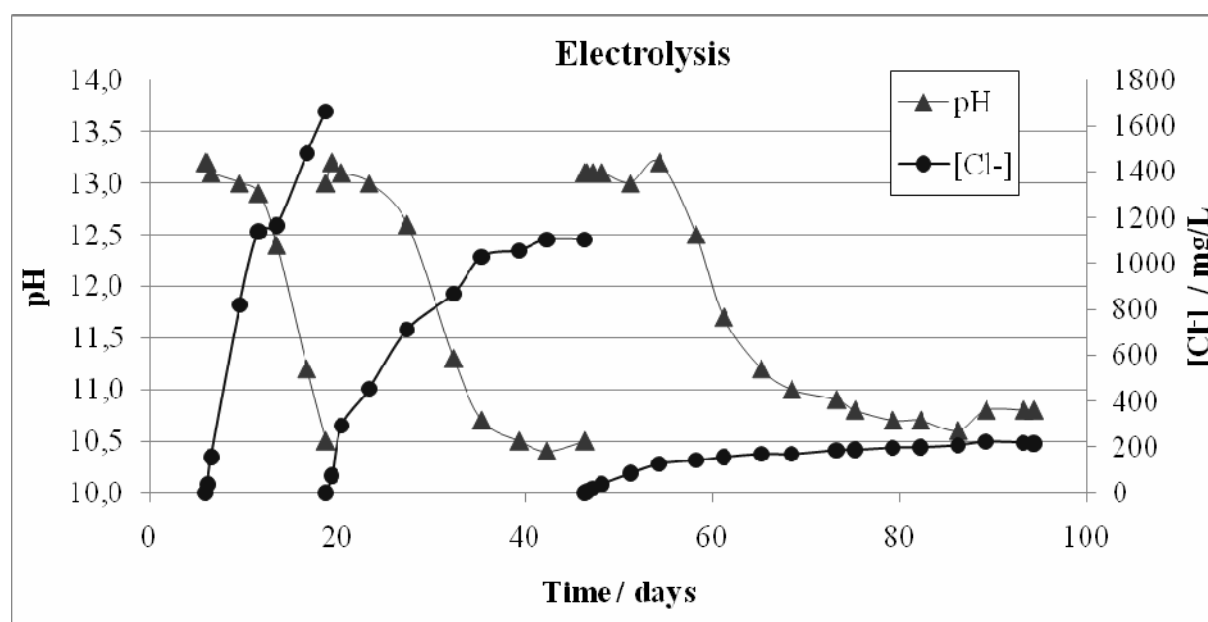

Fig. 1: Evolution of pH and Cl contents during electrolysis of an iron ingot in 10L of KOH (1%w/w).

During the treatments of large objects (for example, cannons), the bath time is longer and the volume of solution is bigger. However the same evolutions of pH and chloride rate are noted (Fig 2.).
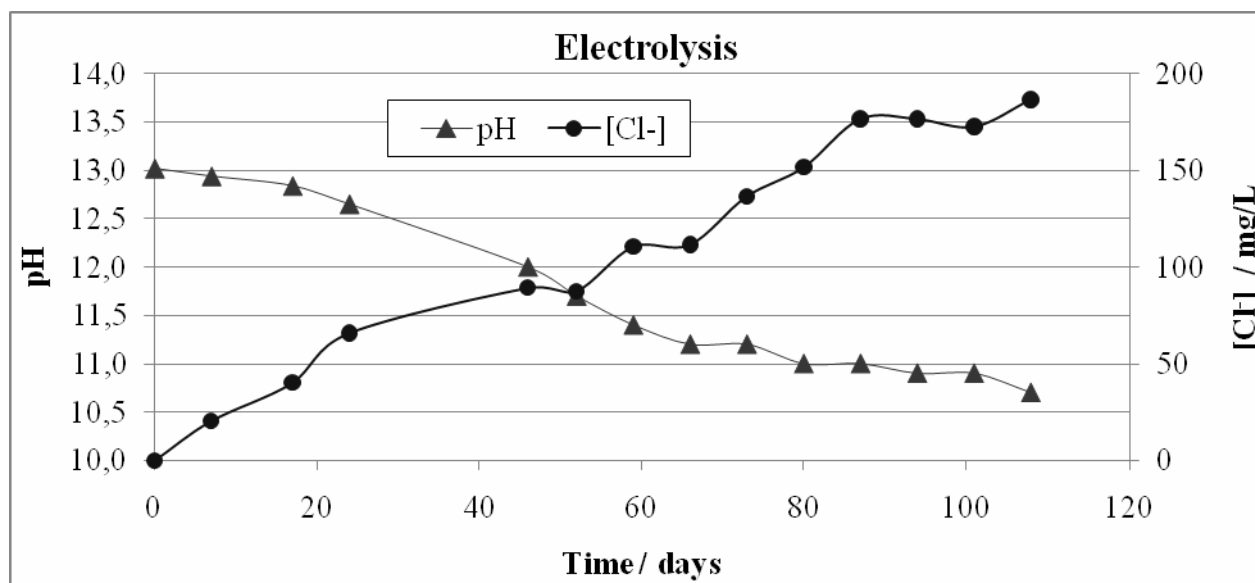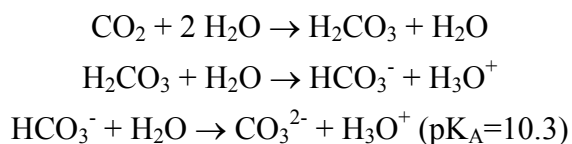
Fig. 2: Evolution of pH and Cl contents during electrolysis of 2 cast cannons (1 cannon from "*Breles*" and 1 cannon from "*Le Juste*" shipwreck (France)) in 3500L of KOH (1%w/w).

In theory, the pH of KOH solution (1 %(w/w) = 0.1782M) is 13.25. With the pH of 10.5, the concentration of OH⁻ is 3.10^{-4}M. If the pH decreases from 13.25 to 10.5, 0.1779M of OH⁻ are consumed, or $2.994.10^{-11}$M of H_3O^+ are produced. During the electrolysis, the production of H_3O^+ could come from the oxidation of water on the anode (stainless steel grid):

$$6\,H_2O \rightarrow O_2 + 4\,H_3O^+ + 4\,e^-$$
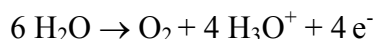
The reactions of carbonation can also produce H_3O^+ ions. Carbonation occurs when carbon dioxide dissolves in water:

$$CO_2 + 2\,H_2O \rightarrow H_2CO_3 + H_2O$$

$$H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+$$

$$HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+ \; (pK_A=10.3)$$

The consumption of OH⁻ could be due to the penetration of anions OH⁻ in the corrosion products of the archaeological object. But normally this phenomenon is limited because the cathodic polarization of the object supports the anions mobility from the object to the solution (the anode).

Currently we don't know which the predominant phenomenon is and how we explain exactly the pH evolution. However the production of H_3O^+ ions (or consumption of OH⁻ ions) is closely dependent on the end of the chloride extraction. Thus it would be possible to use the pH in the monitoring of electrolysis

Immersion treatments in alkaline sulphite solutions

For a research program on the comparison of the iron stabilization, a Roman iron ingot (from Saintes Maries de la Mer, near Marseille in France) was also treated by immersion in 10L of alkaline sulfite (0.5M NaOH and 0.5M Na_2SO_3) at 50°C. The results of pH and chloride rates are showed in the Fig. 3. The pH remains constant and it doesn't depend on the chloride rate. In theory, the pH of the alkaline sulfite solution is 13.7. The measured pH is between 13.1 and 13.7. The variations could be due to the monitoring of solution level (because of the evaporation).
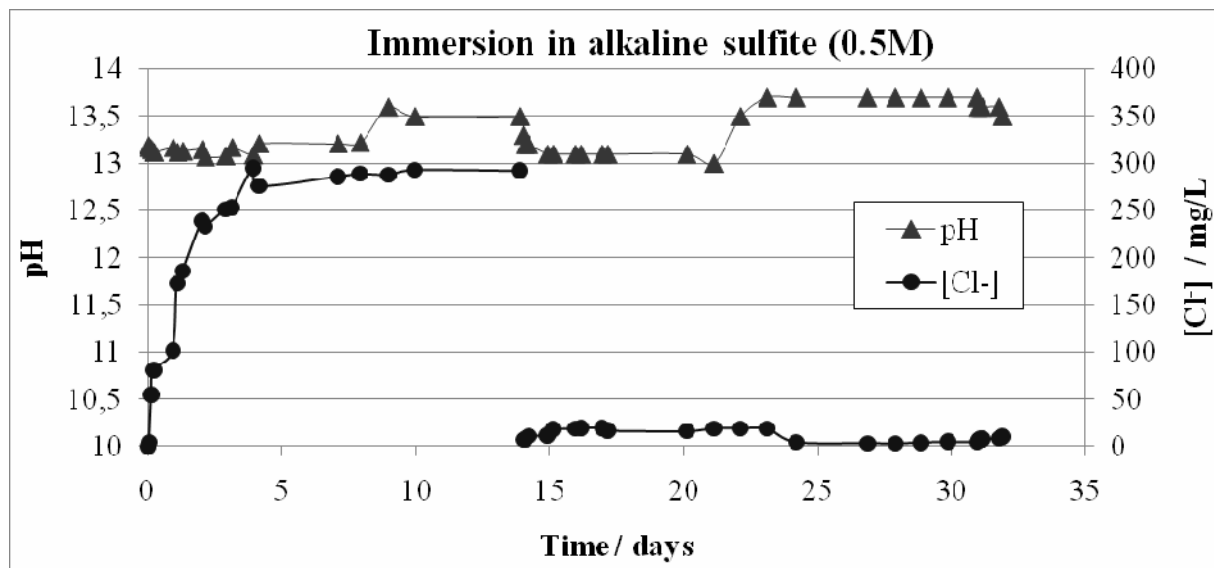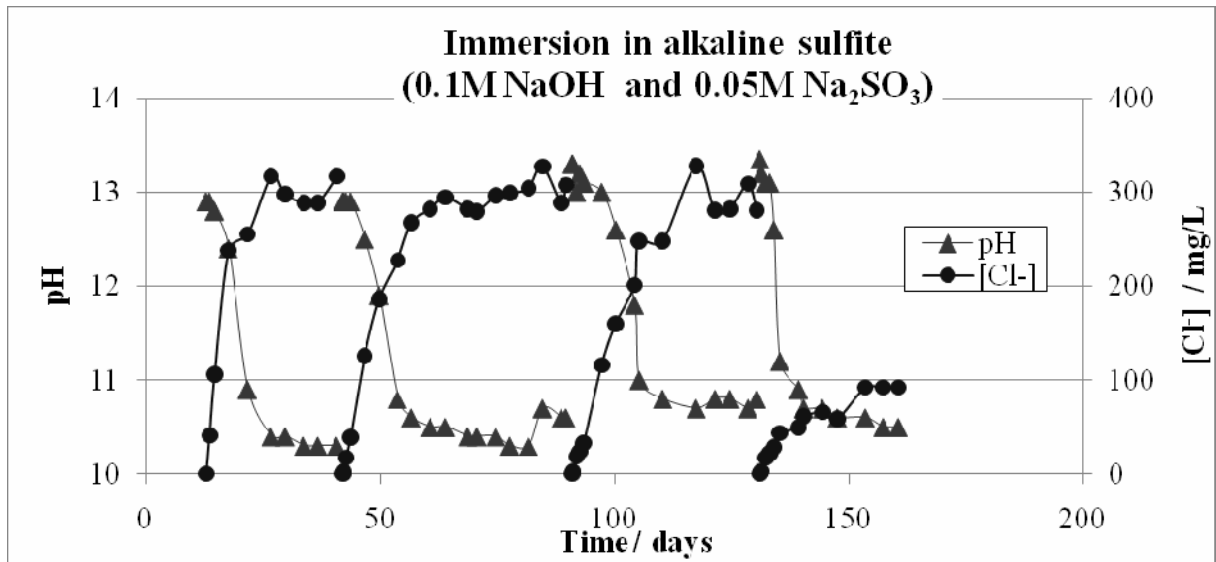

Fig. 3: Evolution of pH and Cl contents during immersion treatments of an iron ingot in alkaline sulphite solutions (0.5M NaOH and 0.5M Na_2SO_3).

Another Roman iron ingot (from Saintes Maries de la Mer, near Marseille in France) was treated by immersion in less concentrated alkaline sulfite (0.1M NaOH and 0.05M Na_2SO_3) at 50°C. The results of pH and chloride rate are showed in Fig. 4. In this solution, the pH decreases from 13 to 10.5. In theory, the pH of the alkaline sulfite solution (0.1M NaOH) is 13. If the pH decreases from 13 to 10.5, 0.0997M of OH^- will be consumed, or $2.99.10^{-11}$M of H_3O^+ will be produced.

We noticed the same evolution of pH during the monitoring of the archaeological artefacts (from *The Natière* site, France) (Fig. 5).

During the immersion in alkaline sulfite, the reactions of carbonation could produce H_3O^+ ions (cf Electrolysis). The diffusion of Cl^- from the object to the solution favours the penetration of anions OH^- in the corrosion products of the archaeological object (Selwyn 2004). If the consumption of OH^- is too big, the concentration of OH^- will not be sufficient to protect iron.

Fig. 4: Evolution of pH and Cl contents during immersion treatments of an iron ingot in alkaline sulphite solutions (0.1M NaOH and 0.05M Na$_2$SO$_3$).
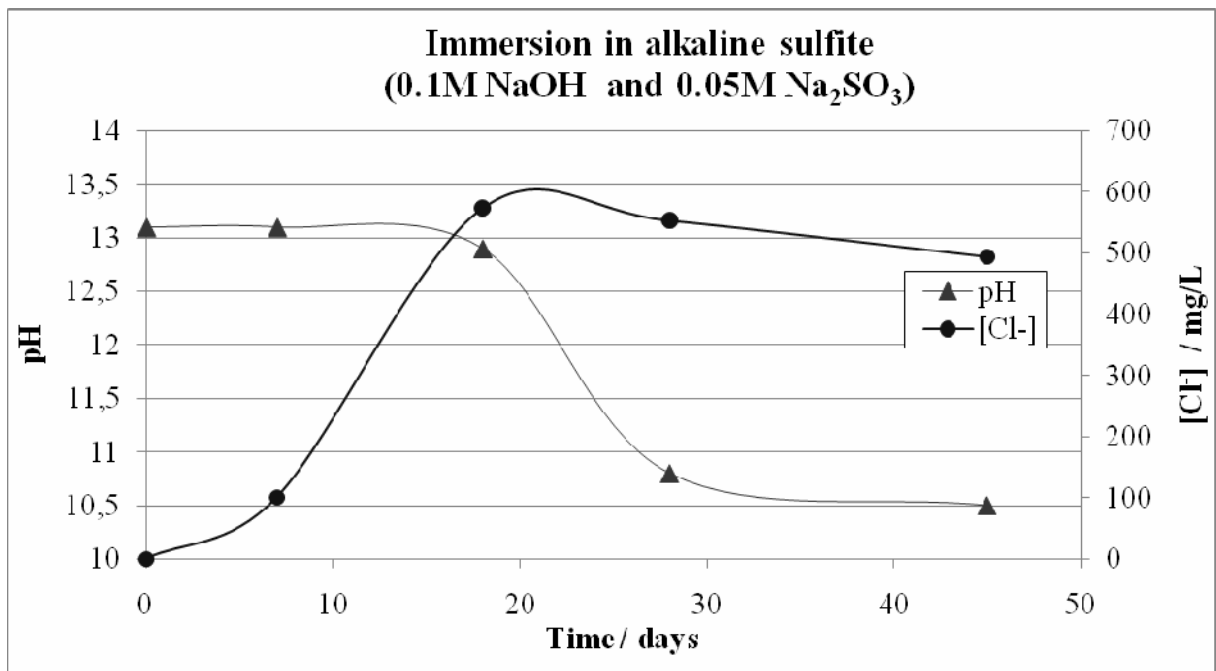
Fig. 5: Evolution of pH and Cl contents during immersion treatments of marine iron artefacts from The Natière site (France) in alkaline sulphite solutions (0.1M NaOH and 0.05M Na$_2$SO$_3$).

Conclusion

Our measurements showed the pH could change during the dechlorination treatments.

In the case of the immersion treatments, the pH only decreases for the less concentrated solutions (0.1M NaOH and 0.05M Na_2SO_3). For the solutions more concentrated (0.5M NaOH and 0.5M Na_2SO_3), the pH is maintained around 13.5. Thus, the quantity ions OH^- would be sufficient. On the other hand, in the less concentrated solutions, the pH decreases to 10. Consequently, this solution would risk to not keeping the domain of iron passive. So, the immersion treatments should be used in higher concentrations (0.5M NaOH and 0.5M Na_2SO_3).

As regards the electrolysis, even if the pH decreases (13 to 10.5), the object is always protected by cathodic polarization. Furthermore, we notice the pH evolution is linked to the rate of chloride extracted: the pH decreases when the chloride rate reaches its maximum value. Thus, it will be possible to use the pH as a means of treatments monitoring. The pH measurement is easiest to use for a routine monitoring of the electrolysis treatments.

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CONSERVATION OF IRON ARTIFACTS FROM THE USS *MONITOR* (1862)

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Over 200 tons of metal artifacts have been recovered from the wreck of the USS *Monitor* (1862), including the ship's engine, condenser, Dahlgren shell guns, and the world's first ship-mounted rotating gun turret. More than 75 percent of this material is composed of wrought or cast iron resulting in the need for large scale evaluation and conservation of iron artifacts at The Mariners' Museum's (TMM) Batten Conservation Lab. The approach taken is a practical one, endeavoring to make optimal use of established treatments and work towards adopting newer, more efficient options when possible.

Conservation of *Monitor* iron artifacts begins with maintaining wet storage conditions from the moment of recovery from the sea until the objects can be safely dehydrated during conservation treatment. Owing to the tremendous volume of material, some of it of a very large weight and volume (engine, 30 tons, turret, 120 tons) this is not an insignificant task. Artifact handling and lifting is a significant challenge due to the size, weight and fragility of many of the *Monitor* components, requiring that an artifact handler with extensive rigging experience is included in the conservation team. Large numbers of artifact tanks are required, some with volumes up to 300,000 liters. Extensive support services such as plumbing and electrical and drainage systems are also needed, as well as fresh water for the storage solutions. In the absence of other complicating factors such as the presence of organic materials, iron artifacts are stored in 1-2% solutions of sodium hydroxide at a pH of 11-13, which serves to prevent significant iron corrosion as well as to begin the process of chloride extraction. Large artifacts have initially been stored in caustic solutions based on tap water for reasons of economy and availability of water purification facilities. Smaller iron artifacts are stored in sodium hydroxide solutions based on de-ionized water. As larger facilities for the production of de-ionized water become available and treatments progess, the large artifacts such as the engine and turret will also be stored in de-ionized water/sodium hydroxide solutions, allowing more effective desalination and reducing the possibility of calcium deposition on the artifacts due to reduced solubility at high pH.

In the case of the gun carriages and turret, current storage is in tap water with the addition of an impressed current cathodic protection system which polarizes the metal sufficiently to prevent significant further corrosion without the addition of an electrolyte. This was done to protect wood elements of the composite gun carriages and to prevent damage to organic artifacts formerly contained within the turret. Now that excavation of artifacts from the turret has been completed, future treatment stages for the turret will be conducted in sodium hydroxide.

The pH, condition and level of the storage solutions are monitored to ensure the best storage conditions possible. The objects are also monitored for signs of corrosion during storage. Frequently, significant amounts of chloride salts are extracted into solution from the objects during wet storage, leading *Monitor* conservators to term this phase of conservation as 'active storage'.

Documentation and cataloguing is continued at this stage, starting with the archaeological context and continuing with pre-treatment, digital photography, computed radiography, measurements and descriptions. Radiography is very important in ascertaining the morphology and level of preservation of the artifact, allowing for careful planning of the conservation and handling. As the appearance changes and true dimensions are revealed during conservation, documentation continues throughout the process concluding with after treatment reports.

The vast majority of marine recovered iron artifacts are covered with a thick layer of 'concretion' (Memet 2007) consisting primarily of calcium carbonate, biofouling, and corrosion products, which must be removed for effective desalination treatment. This is normally accomplished physically with a combination of hand tools and small pneumatic chisels. In some cases the Garcia Method of flame deconcretion has been used successfully on iron artifacts as well (Carpenter 1990). Particular care must be taken when deconcreting objects made of graphitized cast iron, as these have typically lost nearly all of their mechanical strength and may suffer loss easily.

It should be noted that disassembly of multi-component iron artifacts can promote effective release of chlorides from confined spaces, and can also be of great benefit when treating composite artifacts of iron and other metals or organic materials. Disassembly is done when it is possible to do so without causing damage to the artifact (Krop and Nordgren 2010).

Once concretion has been removed and disassembly started, desalination proceeds at a more rapid pace. In some cases this involves passive soaking in 1-2% sodium hydroxide solutions with chloride monitoring at regular intervals of one week, with the solution being changed when chloride concentrations in solution reach a plateau. More often, electrolytic reduction in sodium hydroxide solutions is employed. As well as promoting the release of chlorides, this functions to reduce iron corrosion products and loosen small fragments of remaining calcareous concretion. The treatment solution is often circulated with a pump to promote a rinsing effect and to mix the treatment solution thoroughly before solution samples are drawn for chloride testing.

Chloride testing during iron desalination treatment is normally accomplished by testing samples of the treatment solutions with methods such as chloride ion specific electrodes, potentiometric titration, or ion chromatography. The goal of the iron conservation treatments is to proceed until levels of chloride below 1ppm (mg/L) are measured for at least 3 consecutive weeks. While it is felt that this gives a good indication of the effectiveness of the treatment, it is realized that solution analysis does not tell the whole story and in selected

cases destructive sampling followed by digestion has been performed to look at the quantity of chlorides which may still remain in the metal.

While sodium hydroxide soaking with and without electrolytic reduction are the primary methods currently used for desalination of monitor artifacts, alternative treatments are being evaluated. A study comparing these methods with hot and cold alkaline sulfite washing of *Monitor* iron artifacts was performed by former TMM employee Laura Reid and will be presented separately at this Colloquium. Conservators working on the *Monitor* have followed with interest the development of subcritical extraction of chlorides (de Vivies, Cook, Drews, Gonzalez, Mardikian, and Memet 2007) by the team working on the submarine *HL Hunley* at the Clemson University Restoration Institute and have submitted a sample of wrought iron from the *Monitor*'s turret for subcritical testing.

The use of nitrites for corrosion inhibition, storage and treatment of archaeological iron artifacts is also being investigated and will be reported in a poster session at the Metal 2010 Conference (Sangouard, Nordgren, and Spohn 2010). The test material, sodium nitrite, has the potential to prevent corrosion of iron and other metals such as copper alloys at a near neutral pH, making it an attractive possibility for storage of composite artifacts containing organics or multiple metal alloys. Testing is also underway to determine how well nitrites may function as a medium for extracting chlorides.

Following the removal of concretion, corrosion and significant amounts of chlorides, *Monitor* iron artifacts are thoroughly rinsed in de-ionized water and dried under controlled conditions. A coating of 2-10% tannic acid is applied to protect the surface with an iron tannate layer, followed by coating with clear acrylic coatings. When necessary, components are reassembled and given supportive mountings to relieve stress on the material. The artifacts are carefully monitored in storage and on display, in which the climate is controlled to approximately 50-60% relative humidity (RH) and 20-25 degrees Celsius. It is anticipated that some *Monitor* components may require special display environments such as low RH or modified atmosphere, depending on the extent of desalination treatment that has been achieved.

The general methods and practices described above are used to conserve iron artifacts from the USS *Monitor*. Although this list is not exhaustive, and other methods are utilized depending on certain conditions, these techniques have proved quite effective at stabilizing artifacts recovered from the shipwreck for long term storage and display.

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RETREATMENT OF ARCHAEOLOGICAL IRONS TEMPORARILY SUBMERGED IN BRACKISH FLOODWATERS

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Abstract

Irons artifacts excavated at Jamestown, Virginia, USA, (Fig. 1) between 1930 and 1950 led chemists to coat the artifacts with layers of parrafin wax. Salt from the floodwaters entered into the abraded wax layers and on the surfaces of the irons causing ferrous oxide corrosion. Treatment precluded dewaxing in 20 liters of xylene in a solvent still heated at 350°F, 176°C for 6 to 8 hours; desalination in 1 percent of NaOH and deionized water; application of 5 percent tannic acid mixed with deionized water; and a coating of 10 percent paraloid in a solution of 50 percent each xylene and ethanol.

Challenges throughout the phases of treatment included wax on the surface of the irons after the dewaxing process. Residual wax forced conservators on the project to retreat the artifacts by xylene immersion at room temperature for 24 to 48 hours. Desalination often yielded weekly volatile chloride readings in treatment batches; the objective being the stabilization of the level of chlorides in the solution at 10 parts per million (ppm) over a four week period.
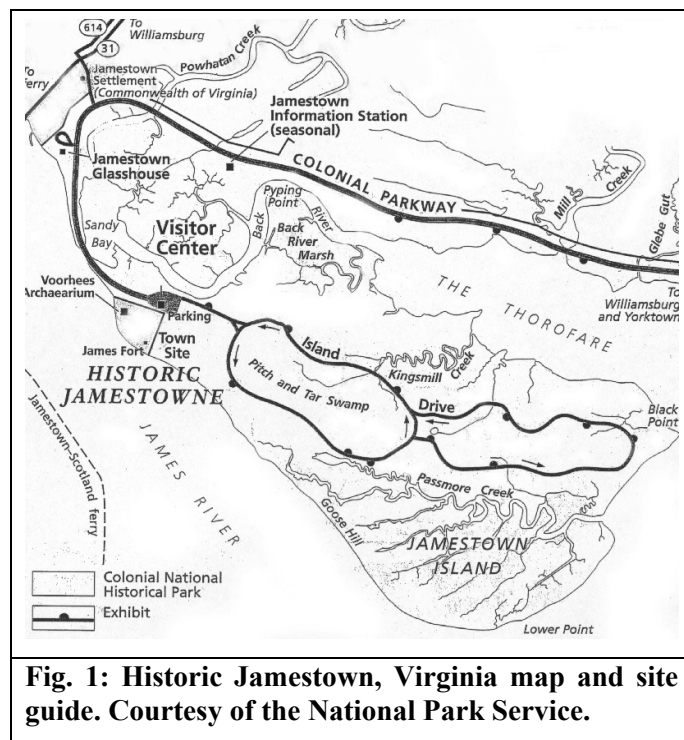
Fig. 1: Historic Jamestown, Virginia map and site guide. Courtesy of the National Park Service.

Two four week periods of abherrant readings delegated immersion into plain deionized water instead of the NaOH solution. The immediate results revealed the desired level of 10 ppm between a 1 to 4 week period. Tannic acid application acted as a stabilizer to the corrosion resulting in the change of the orange rusted color of the irons to their original black appearance. Some objects, however, were resistant initially to the first application and required spot mechanical removal before a secondary tannic acid application.

Extended Abstract

In 2003, Jamestown staff members prepared the site storing the object for the onslaught of Hurricane Isabel in accordance to its emergency plan. Unfortunately, the combination of the hurricane and its related storm surge brought in waters from the nearby Pitch and Tar Swamp (which takes in waters from the James River) measuring 5 ft, 152 cm deep at the National Park Service (NPS)Visitor Center. A significant number of the 900,000 artifacts were affected. 42,500 of them, including approximately 20,000 iron objects, were sent to the lab as an agreement between the National Park Service and the MAC lab in 2004.

The iron artifacts were treated with paraffin wax applied as both a consolidant and protective coating by the Civilian Conservation Corps (CCC) and National Park Service in 1935. The original wax treatment would remain on the irons until their retreatment at the Maryland Archaeological Conservation Laboratory (MAC) in St. Leonard, Maryland. Although the wax from the previous treatment offered some protection, the irons suffered corrosion from the fissures in the wax that developed over several decades. Consequently, these openings allowed salt laden waters to enter the surfaces of the objects.

The James River situated near 540 km to the southern portion of the Chesapeake Bay, is a large watershed stretching from New York to Virginia. Salinity levels in the James river are affected by the urbanization and farm land use around the bay (Benke, et al., 2005) Runoff waters originating from the rainfall in these areas create groundwater containing nitrates and chemical contaminants adversely changing its saline properties. Studies conclude that 48 percent of the nitrates found in groundwater contribute to the contamination of the James River.

Hurricane Isabel brought 1,190 billion gallons of groundwater between September 19-25, 86.9 billion gallons per day (329.4 billion liters), which is 8 times more than the normal amount of rainfall to enter the Chesapeake during a 7 day period in September (USGS, 2003).

The James's highest saline counts were recorded at 15 ppm on September 24, 2003 based on information from a stationed buoy in the river (Virginia's Department of Environmental Quality, 2003). In March 2004, samples were taken at Jamestown by NPS staff members showing readings between 40–88 ppm, a significant increase from the readings taken during the storm. The Pitch and Tar swamp adjacent to the visitor center measured 157-276 ppm during the same time period.

Irons submerged for a minimum of 24 hours into floodwaters from the swamp were made susceptible to these same contaminants and augmented salinity which ultimately led to their corrosion. Jamestown staff and NPS volunteers rinsed the irons in distilled water and bagged them in two other holding facilities before the objects were sent to the MAC lab.Upon their arrival, conservators commenced the first phase of treatment, dewaxing followed by desalination. A typical batch of irons consisted of 200-300 objects per bin. Chloride readings taken from these batches concluded a range of 10-15 ppm during the first week immersion.

Alkaline solutions tend to dissolve both organic and inorganic material while producing an environment where corrosion substances are pliable, allowing an easier removal of Cl^- ions High temperature in alkaline solutions increases the solubility of iron oxides forcing more of the corrosion products to dissolve (Selwyn and Argyropoulos, 2005). The lab's relative humidity (RH) averaged at 65 degrees farenheit, 18 degrees celsius daily, however, there are periods of increased RH during the summer season.

A majority of the chloride readings were heightened for several months possibly indicating continued states of corrosion caused by an attraction between Cl^- and Fe^{+2} ions.

The adsorption of Cl^- ions is also contingent on the pH of the solution. If corrosion is passivated at a high pH, the presence of Fe^{+2} ions are decreased minimizing the attraction between the two. In acidic conditions, Cl^- ions are adsorbed into iron oxide surfaces of the object at a retarded rate because the charge on the Fe^{+2} becomes Fe^{-2}, repelling the Cl^- ions. (Selwyn and Argyropoulos, 2005) In these cases, the results were lower chloride readings.

Because chloride test results fluctuated weekly revealing both high and low readings, questions regarding the pH of the lab's deionized water became a factor. It was found that the pH level was measured above 7.0. Furthermore, 1 percent NaOH solutions exhibited ranges between 12.0 and 18.0pH. 60 percent of the objects in desalination contained chlorides ranging 30-64 ppm weekly. Irons were removed from these solutions and placed in deionized water in an effort to deactivate any remaining chlorides. Weekly test results yielded lower chloride readings.

The initial treatment proposed by lab conservators stipulated a final coating of paraloid. In order to prevent reactivation of corrosion within a microenvironment, objects in high chloride solutions did not receive an application of paraloid.

The wax layers that remained on some of the irons prevented tannic acid application from being effective. About 2 percent of the last 3,000 objects remaining in treatment required additional xylene immersion at room temperature for 24, 48, and 72 hours. Most of these objects responded to the second xylene treatment and reacted positively to the tannic acid application. In other cases where the wax remained on the surfaces, tannic acid applications were again unsuccessful. It was not advisable to perform a tertiary xylene treatment due to the fragile and mineralized state of the objects.

References

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