RESEARCH

The use of gels in localized dechlorination treatments of metallic cultural heritage objects

Clémence Fontaine, Stéphane Lemoine, Charlène Pelé-Meziani and Elodie Guilminot[*]

Abstract

Gels were used to perform localized dechlorination treatments on ferrous or copper alloy archaeological objects. Agar gel ($3\%_w$) was used as a medium for the electrolyte, a $1\%_w$ KNO_3 solution. Localized electrolysis with gel was carried out using the same parameters as immersion electrolysis. To determine the end of treatment, two tools were validated: determining the quantity of chlorides present in the gels by XRF and monitoring the oxygen consumption of an object before and after treatment. This study shows that the technique results in the efficient extraction of chlorides. In the case of the stabilization of composite objects or for the localized treatment of copper objects, the use of a localized electrolytic gel treatment is a new effective solution proposed to conservators.

Keywords: Gel, Curative treatment, Electrolytic dechlorination, Iron, Copper alloys

Introduction

After excavation, metallic, iron or copper alloy objects are highly reactive. The presence of chlorides in the burial environment initiates cyclic corrosion that is reactivated by excavation due to an increase in oxygen levels. Whether for ferrous or copper objects, corrosion processes involve redox reactions. The oxidation reaction is that of the oxidation of the metal, while the reduction reaction is due to the reduction of oxygen. These redox reaction determine the rate of degradation of the object. Thus, oxygen is a key factor in the corrosion and decay of metallic artefacts. In the case of iron, the damages arise from the extreme reactivity of the chlorinated corrosion product layer developed on the artefacts [1, 2]. Two main Cl-containing phases are identified: the akaganeite: β-FeOOH and the hydroxychloride β-Fe$_2$(OH)$_3$Cl [2, 3]. The formation of new chlorine-containing phases within the corrosion system generates and amplifies the spectacular post-excavation degradations observed on ancient metallic objects [1]. The fast artefact degradation following these processes is irremediable: cracking, swelling of the corrosion layers, these phenomena can lead to the complete destruction of archaeological objects within a short timeframe. For copper alloys, chlorides are inside the passive (protective) patina and they are also observed, on the other hand, at the interface alloy/patina, where they often induce fundamental instability and disruption of the patina [4–6]. Consequently chloride anion can be involved both in processes conducting to the formation of stable patina and to those in which severe corrosion occurs. Active corrosion is generally more localized although it risks undermining the overall conservation state of the object. Over many years, dechlorination treatments have been developed to effectively stabilize ferrous or copper alloy objects: these treatments are generally chemical [7–11] or electrochemical [12–16]. They require the object to be totally immersed in an alkaline solution. They are appropriate for objects made of a single material, even if they sometimes present risks for the patina of copper alloy objects. However, these treatments are unsuitable when ferrous or copper alloys are associated with other materials, such as organic materials (wood, leather, textiles, bone, horn) [17]. The treatment of composite objects is always a real challenge. Often the treatment of one material is privileged to the detriment of the others, and the treatment of the composite object

*Correspondence: Elodie.Guilminot@Loire-Atlantique.fr

Arc'Antique, Grand Patrimoine de Loire Atlantique, 26 rue de la Haute Forêt, 44300 Nantes, France

becomes a series of compromises rather than an ideal solution. Composite objects require localized treatment, but this is not always possible with current techniques. An existing tool that has been developed to perform localized electrochemical treatments is the Pleco electrolytic pencil [18]. The electrolytic pencil is particularly suitable for the localized cleaning of silver tarnish. Silver sulfides are rapidly reduced, with good control of parameters. Dechlorination requires longer electrochemical treatment times on different surface sizes. The Pleco is unsuitable for localized electrochemical dechlorination treatments. Localized electrochemistry is also used in cultural heritage to characterize protections [19]. Ramirez Barat et al. [19] carried out electrochemical measurements (EIS and Rp) of patinas before, during and after gel-electrolyte cell conservation treatments on a bronze sculpture. Their work validated the effectiveness and applicability of an agar gel polymer electrolyte cell in electrochemical measurements. They demonstrated the practical advantages of gel to control electrochemical parameters on a real object. The use of gels in treatments is widespread for paintings, paper and graphic arts [20–24], but much less frequent for metal cultural heritage artefacts. An initial study has shown the interest of gels in the chemical cleaning of metal objects [25]. Agar gels are particularly suitable for metal objects with non-flat surfaces. A hot application of peelable gels (such as Agar) ensures good contact between the metal surface and the gel.

The objective of this paper is to present localized electrolytic treatments by gel. Localized dechlorination treatments were performed on iron or copper alloy archaeological objects. Description of the treatment will be followed by evaluation using a series of different analysis techniques.

Results and discussion

Dechlorination treatment by gel is a similar process to an immersion dechlorination treatment. The electrochemical setup was a classic 3-electrode electrolysis setup. The object to be treated was used as the working electrode. The gel (Agar 3%w/w with KNO_3 1%w) acted as an electrolytic solution and the counter electrode was a stainless-steel grid. The reference electrode was placed in an extension containing a conductive solution (KNO_3 1%w), inserted in the gel (Fig. 1). The reference electrode was a saturated calomel electrode (SCE). Cathodic potential was applied to the object to be treated (working electrode) to allow chloride ions to migrate into the gel.

The first treatment test was performed on a fragment of an iron ingot (treatment time of 2 h at -1.04 V/SCE). The sample was observed by EDS-SEM after electrochemical treatment (Fig. 2). The mappings clearly showed
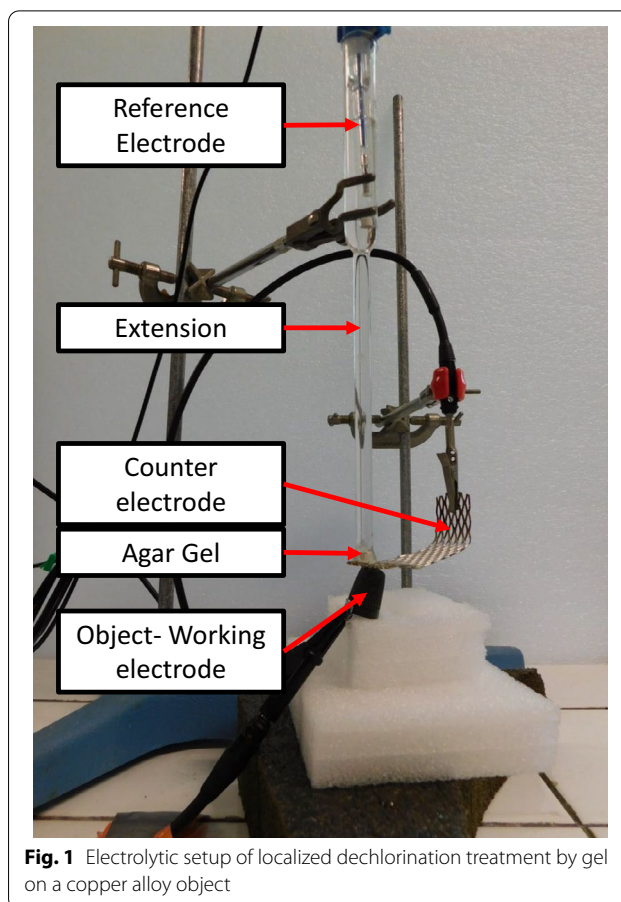

Fig. 1 Electrolytic setup of localized dechlorination treatment by gel on a copper alloy object

the presence of residual chlorides at the metal/corrosion product interface. Electrochemical treatment by gel extracts chlorides in the same way as electrochemical treatments by solution. The difficulty was to determine the end of the treatment. Dechlorination treatment (whether by immersion or electrolysis) is generally followed by the measuring of chlorides, with a sample being taken from the treatment solution [12]. In the case of electrochemical treatments by gel, it is impossible to take samples to measure chloride during the treatment. The determination of chlorides is carried out on the gel by p-XRF, after treatment (procedure described in materials and methods).

The first treatment parameter studied was the duration of treatment application. Tests were carried out on fragments of an iron ingot with varying treatment times: 30 min, 1 h, 2 h or 4 h. The respective post-treatment quantities of chlorides in the gels are presented in Fig. 3. The results did not establish a correspondence between the amount of chloride extracted and a longer treatment time. The greatest amount of chloride extracted corresponded to the shortest treatment time: 30 min. Since the tests were carried out on fragments of the same ingot,
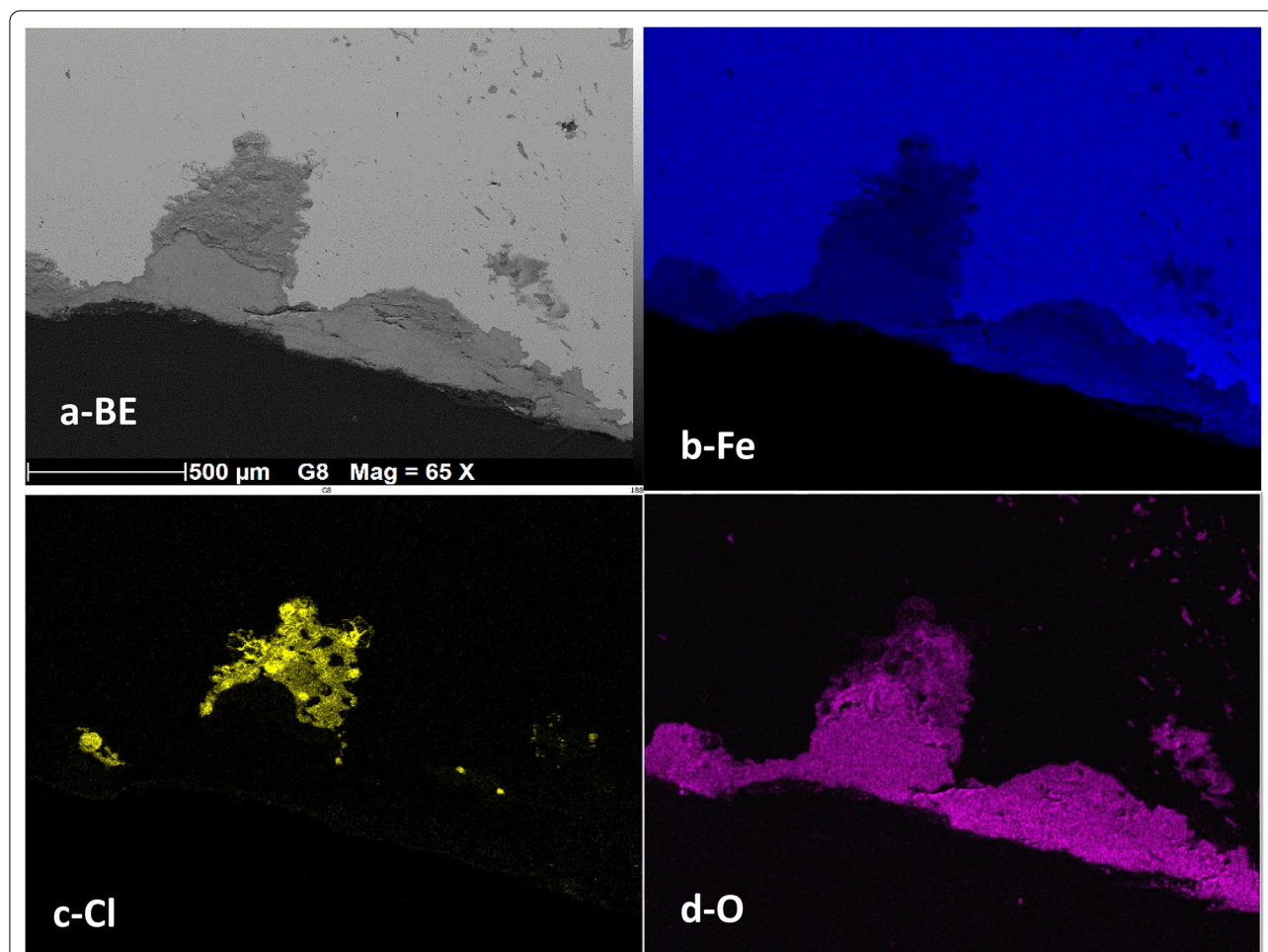
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Fig. 2 EDS-SEM observation of an iron ingot fragment electrochemically treated with a 3%w/w Agar gel with 1% KNO_3 1%w at -1.04 V/SCE for 2 Hours: **a** Photo in Backscattered Electron (magnification × 65), **b** mapping of the Fe, **c** mapping of the Cl, **d** mapping of the O

it would seem probable that there were variations in the amount of chloride in different areas. However, in these experiments, it was observed that the longer the treatment time, the more contact was lost between the gel and the object's surface due to the gel drying. To optimize contact between the gel and the surface of the object, a drop of solution (KNO_3 1%w) was placed on the surface before applying the gel and electrochemical treatment was limited to 30 min. These conditions ensured good contact between the gel and the surface of the object, and facilitated control of the electrochemical treatment parameters.

To determine the effectiveness of the treatment and the end of dechlorination, other electrochemical treatments were carried out on a set of copper alloy objects with localized corrosion (Object 2020373, 2020374 and 2020378 described in materials and methods). On each object, 1 to 3 areas were considered to be active corrosion areas and were treated. The gel was applied to the

localized corrosion area to extract chloride at a potential of − 0.192 V/SCE for 30 min. The treatment was repeated on each area 5 to 7 times. The post-treatment quantity of chlorides in each gel was measured by p-XRF. To evaluate the reactivity of the object, oxygen consumption was measured for each object before and after treatment. The measurement of oxygen concentrations and the quantification of oxygen consumption are therefore extremely useful indicators for both corrosion and conservation science. A very efficient tool to evaluate the effectiveness of a treatment by measuring oxygen consumption has been developed and applied in conservation [26]. The procedure used is described in materials and methods.

On Object 2020373, area 1 was largely treated (7), while on areas 2 and 3, there were 5 applications of gel with electrolysis. Measurement of chloride in the gel indicated that chloride extraction was rapid in area 3, since after only the 2nd application of gel, the quantity of chloride
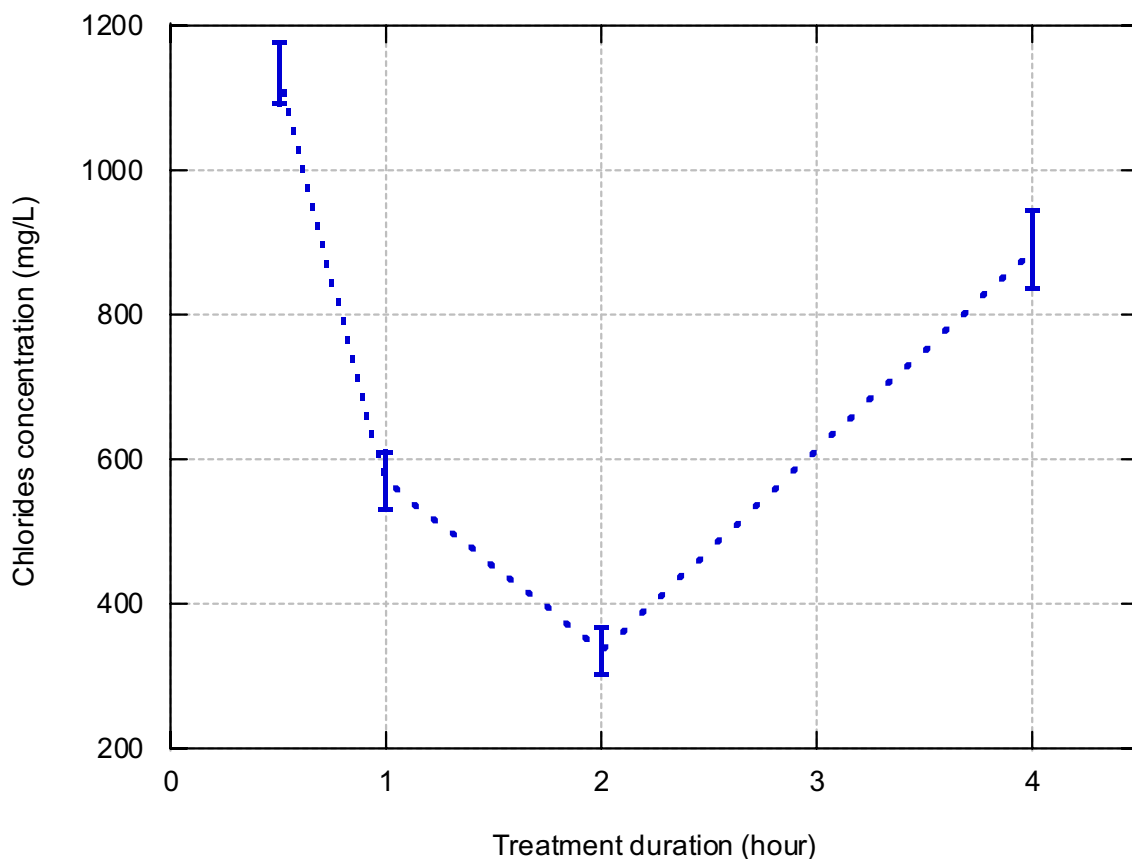
Fig. 3 Determination of chlorides in gels used in the dechlorination of an iron ingot fragment electrochemically treated with a 3%w/w Agar gel with 1% KNO$_3$ 1%w at -1.04 V/SCE with treatment times of varying durations

was negligible (Fig. 4). For area 2, the quantity of chloride did not become negligible until the 4th application. For area 1, chloride extraction was more variable, but was considered complete after the 7th application. End of treatment was determined by oxygen consumption measurements: oxygen consumption was 4%/day before treatment and dropped to below 1%/day after treatment (Fig. 5). This oxygen consumption rate is equivalent to that measured on a treated coin protected by a varnish (Object 2021045 in Fig. 5). Object 2020373 can thus now be considered as stabilized.

Close-up of Fig. 4

For the thimble (object 2020374), 2 areas were treated with 6 applications on each area. For Area 1, the monitoring of the chloride rate shows a decrease in the chloride rate in line with the number of applications, while for Area 2, the chloride rate is more variable (Fig. 4). Based on the gel chloride rate data, it is difficult to affirm that the object is completely stabilized. Oxygen consumption rate decreases after treatment (Fig. 5), but it remains higher than that observed

on Object 2020373: oxygen consumption was 15%/day before treatment, and 9%/day after treatment. The oxygen consumption measurements and the chloride rate in gels after treatment for Object 2020374 show that dechlorination is incomplete, and treatment should therefore be continued.

For the clamp (Object 2020378), 2 areas were treated with 7 applications on the first area and 5 applications on the second area. For Area 1, the chloride rate was variable, but remained low (Fig. 4). For Area 2, monitoring of the chloride rate shows a significant decrease, and the chloride rate became negligible from the 3rd application of the treatment. Chloride measurement data on post-treatment gels indicate that chlorides were extracted from the 2 areas treated. Oxygen consumption rate decreased after treatment (Fig. 5), but remained very high: oxygen consumption was 94%/day before treatment, and 25%/day after treatment. Such high oxygen consumption measurements indicate that corrosion is still active and chlorides are still present in the object. In fact, the two treated areas are both located on the external surfaces of
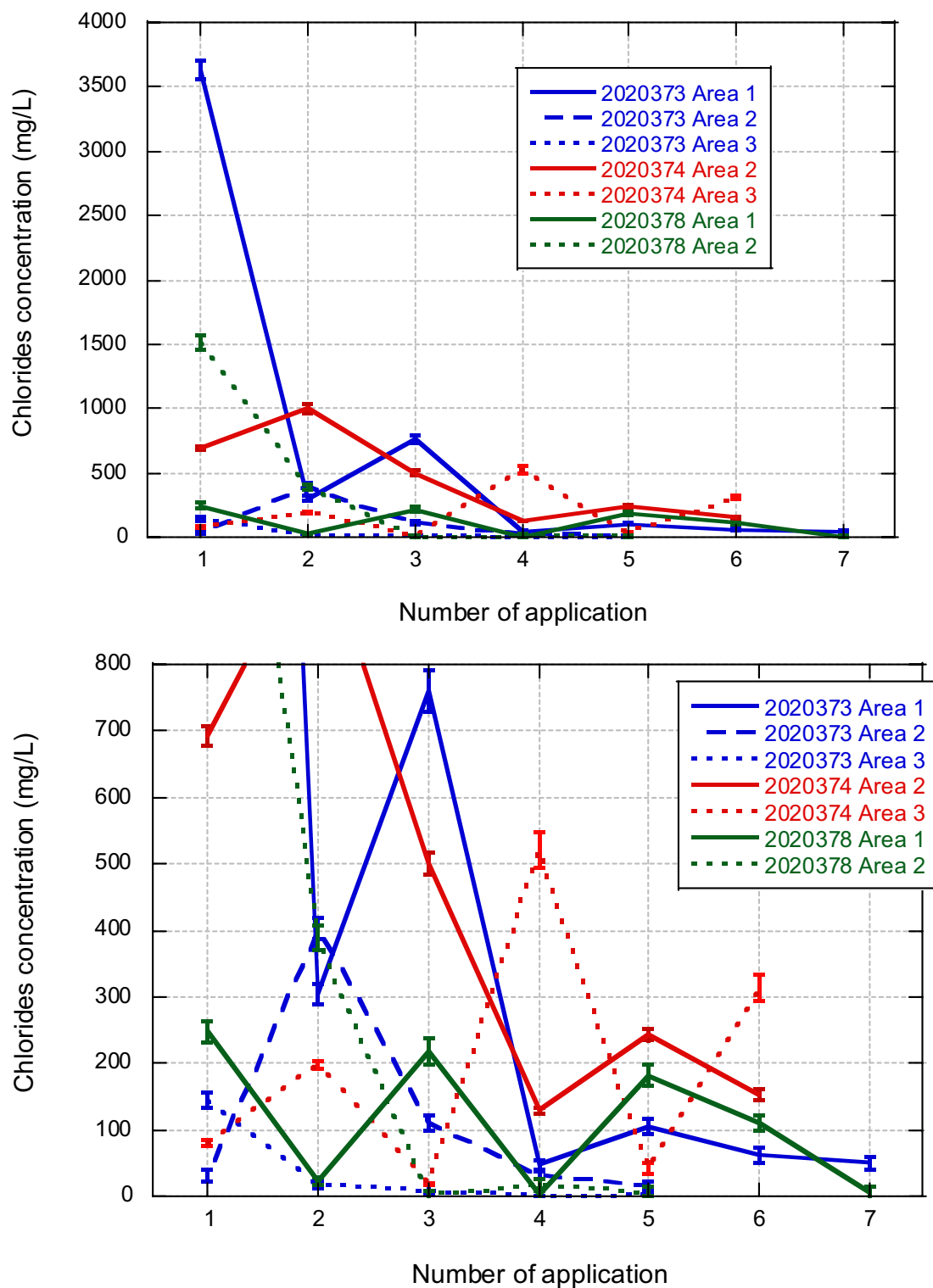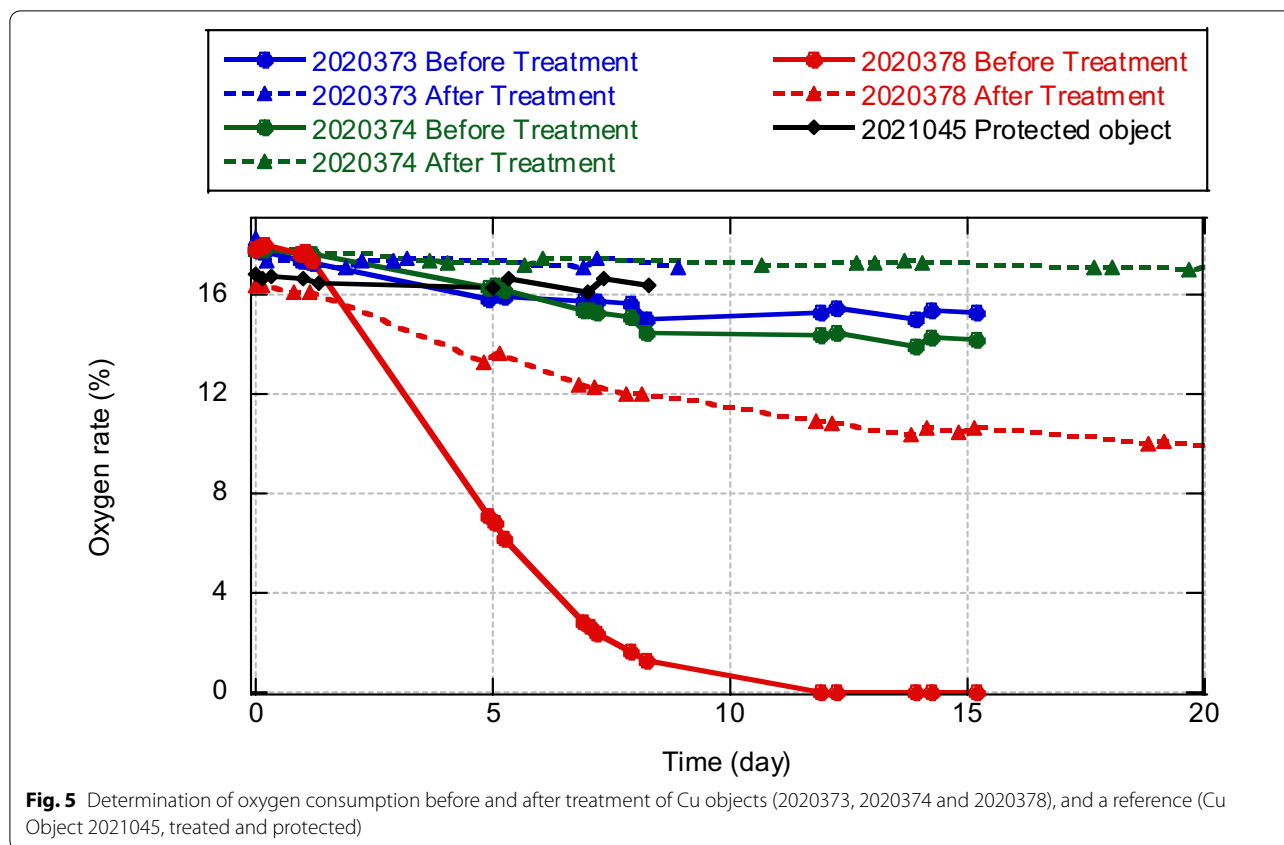
Fig. 4 Determination of chlorides in gels used for the dechlorination of Cu objects (2020373, 2020374 and 2020378) electrochemically treated with a 3%w/w Agar gel with 1%w KNO_3 at − 0.192 V/SCE

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Fig. 5 Determination of oxygen consumption before and after treatment of Cu objects (2020373, 2020374 and 2020378), and a reference (Cu Object 2021045, treated and protected)

the clamp. However, there are also corroded areas on the internal surfaces of the clamp requiring treatment, but it is difficult to carry out dechlorination using electrochemical treatments on these areas.

The results obtained on the different iron or copper alloy objects show that electrochemical treatments by gel are effective for the local extraction of chlorides and stabilizing the objects. The treatment must be repeated until the chlorides are completely extracted. In order to determine end of treatment, it is necessary to determine the chloride rate in the gels after treatment as well as the oxygen consumption of the object before and after treatment. These two techniques are complementary: the measurement of chlorides in the gels after treatment ensures that the area has been completely treated, whereas the oxygen rate is a more global measurement that verifies that there is no active corrosion on the object. In some cases, such as Object 2020373, the chloride rate and oxygen consumption measurements indicated that the stabilization treatment was complete. Monitoring may appear to be repetitive, but in other cases, such as the thimble (Object 2020374), chloride rate measurements are low but fluctuate. Oxygen consumption measurements are essential to confirm whether treatment can be stopped or should be continued. But measuring the oxygen rate as the only

monitoring tool is not sufficient: in the case of the clamp (object 2020378), measuring the oxygen rate showed that the object was still active. It was of no use to continue the treatment on the 2 areas of this object because measurement of the chloride rates in the gels after treatment showed that all chlorides had been extracted from the two areas. The remaining chlorides are, in fact, in an area that is difficult to access (on the inside of the clamp).

Conclusions

This study proposes a new treatment technique for the localized dechlorination of iron or copper alloys. Treatment parameters were optimized. Chlorides were extracted from the treated areas delimited by the application of the gel. The gel contained the electrolyte, a solution of KNO_3 at 1%w. Treatment duration was limited to 30 min to avoid loss of contact due to the drying of the gel. For dechlorination to be complete, it was necessary to repeat the treatment several times, changing the gel. The number of applications was determined by measuring the rate of chlorides present in the gels after treatment. Treatment was monitored by measuring the oxygen consumption of the object before and after treatment. These protocols ensured the stabilization of the object.

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This new localized gel dechlorination treatment requires control of electrochemical treatments but also access to analysis techniques such as p-XRF and O_2 sensors to ensure effective monitoring.

Despite these constraints, these treatments can be very useful for objects that are currently very difficult to treat, such as composite objects. The treatment protocols proposed in this paper should allow conservators to successfully carry out local dechlorination on ferrous or copper objects.

Materials and methods

Corpus

The first objects (Fig. 6) were fragments of iron ingots from a Gallo-Roman wreck (first century AD) found off the coast of Saintes-Maries-de-la-Mer in the Camargue in 2003. Various ingots were excavated in 2005, 2006 and 2008.

The 4 copper alloy objects studied come from an excavation at Saint-Cast-le-Guildo in the Côtes-d'Armor, by the DRAC of Bretagne in September 2020 (Fig. 7). Object 2020373 is a handle. Object 2020374 is a thimble. Object 2020378 is a clamp. They have localized active corrosion areas. Tests of localized treatments were carried out on the zones of active corrosion (outlined in red in Fig. 7).

A copper alloy coin (reference 2021045) from excavations at Allonnes in the Sarthe, under the direction of INRAP, was treated in March 2021 (Fig. 8). This coin was cleaned mechanically then protected with a corrosion inhibitor (immersion of 24 h in an alcoholic solution of benzotriazole (BTA) (30 g/L.)) and by the application of an acrylic varnish (Paraloid B72 in acetone, 50 g/L).
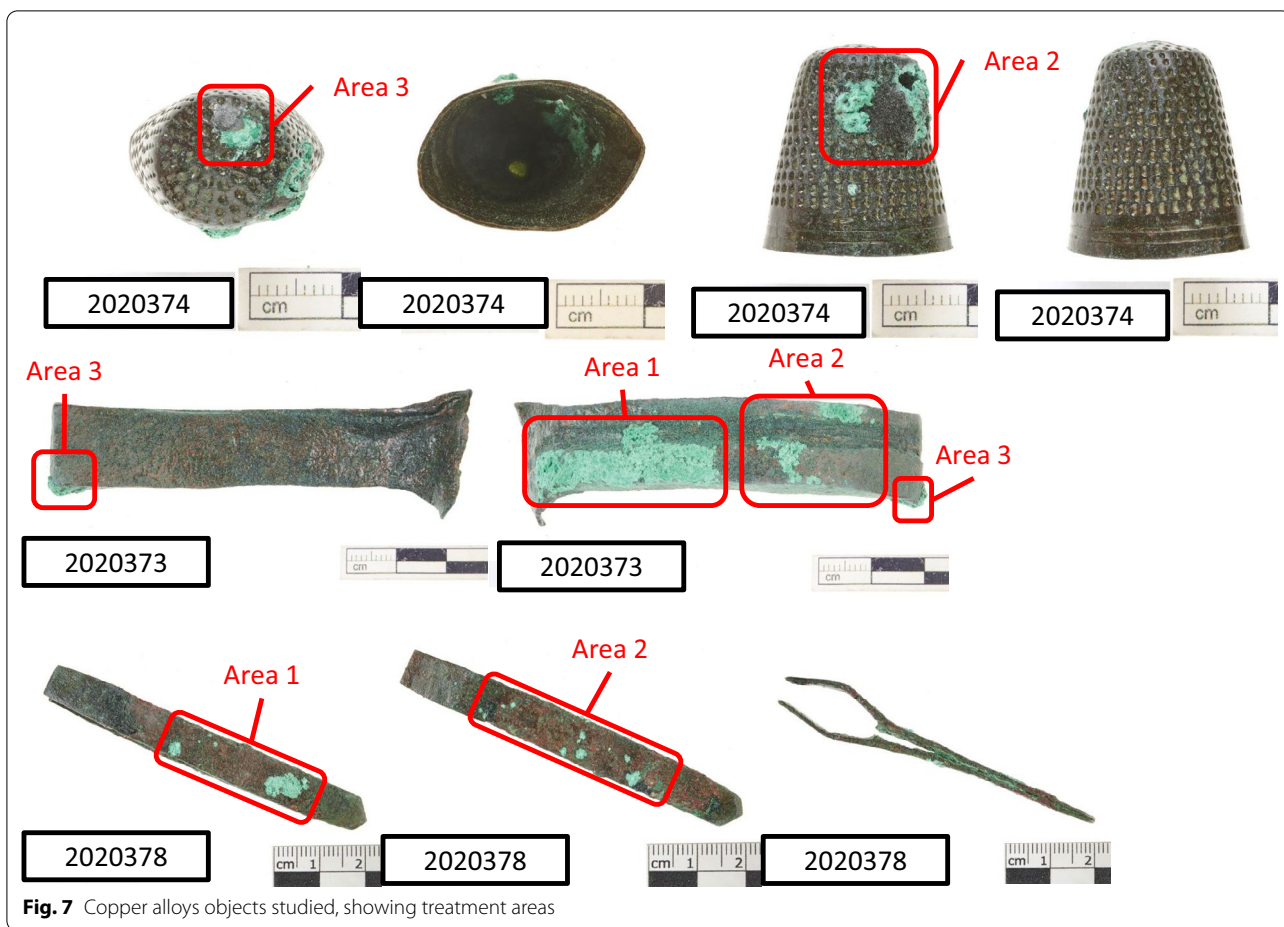
Materials

Preparation protocol of gel: Agar Art® 3%w

For hot application with a syringe: heat the treatment solution (KNO_3 1%w) to 50 °C before slowly stirring in the Agar Art® powder at a concentration of 3%w (Agar provided by CTS). Heat to 90 °C until the mixture becomes homogeneous and translucent. Allow to cool for 24 h before heating a second time to 90 °C.

Fig. 6 Fragments of iron ingots from a Gallo-Roman wreck (first century AD)

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Fig. 7 Copper alloys objects studied, showing treatment areas

Fig. 8 Copper alloy object already treated

Electrolytic setup

Electrochemical treatments were carried out by potentiostat, Origalys EIS-OGS 100 and Origa master 5 software.

Analysis techniques

EDS-SEM analysis

Iron samples were embedded in a cold-mounting epoxy resin and polished with a series of silicon carbide papers

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down to 4000 grit and with 1 μm diamond paste. Samples were carbon coated. They were examined by SEM–EDS: Scanning electron microscopy (SEM) (JEOL JSM 5800LV) was used at 20 kV to observe the morphology of corrosion products, and energy-dispersive x-ray spectroscopy (EDS) (SAMx) to determine the elemental composition.

p-XRF analysis technique

Chloride determinations in gels were performed with a portable XRF instrument (Tracer—Brucker) with a 4×3 mm analysis window and a vacuum system for the detection of light elements, with tension at 40 kV and current at 13μA. The duration of each analysis was 60 s. S1PXRF software was used to perform the analyses and Brucker Spectra software was used to analyze the resulting spectra and to link the peaks in the spectra to the corresponding elements. Precise determination of chlorides in the gels was performed by the standard internal method (K peak, produced by the 1% KNO_3). Calibration curves were plotted with the ratio of the area under the Cl peak to the area under the K. The detection limit of Cl is 0.01 ppm.

Oxygen sensor

Oxygen consumption was measured with an O_2 sensor and a PreSens device (Fibox 4). The object was placed in a waterproof ESCAL pocket (from Long Life for Art) with a relative humidity of 90%, maintained by means of a water / glycerol mixture [27]. The size of the pocket should be at least twice the size of the object studied (Table 1).

If the pocket is too large, oxygen measurements will be inaccurate, but if it is too small it will be difficult to reuse after dechlorination, because it is sealed for each experiment, and must therefore be cut to take the object out. To determine the pocket's precise volume, it is folded and the sensor is attached with silicone glue to the side opposite the opening. Then the object being studied and 1 mL of the glycerol/water mixture (for pockets up to 1000 cm³, after that more solution is needed) are inserted and the pocket is

sealed. The oxygen level is measured twice a day and its evolution over time is recorded. Although the phenomenon of oxygen consumption by a corroding object is not totally linear, the linear part of the curve of the oxygen level versus time is modeled by a straight line whose slope should be observed. The "normalized" oxygen consumption rate can be deduced by means of the following calculation:

$$Normalized\ oxygen\ consumption\ rate = \frac{Volume_{pocket} \times slope}{Volume_{object}}.$$

The value obtained does not represent a real physical phenomenon and is only useful for the purpose of comparing two objects, and is particularly of interest for comparing an object before and after treatment.

Table 1 Object and pocket volumes for oxygen consumption measurements

Object	Volume of object V_{object} in cm³	Volume of pocket before treatment V_{pocket} in cm³	Volume of pocket after treatment V_{pocket} in cm³
2020373	5	98	72
2020374	1.1	60	49
2020378	1.4	68	84
2021045	4		37

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