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Effectiveness of Electrolytic Treatment in Achieving Stability of Archaeological Metals: A Laboratory and Applied Study

Aalaa Saihi[1], Sebati Mourad[2]
[1]Higher School for Teachers “Taleb Abderrahmane”, Laghouat, Algeria
EMAIL : a.saihi@ens-lagh.dz
[2]University Center Aflou , Algeria
EMAIL: m.sebati@cu-aflou.edu.dz

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Abstract:
This study presents an in-depth experimental investigation of the electrolytic method (Electrolytic Reduction / Cathodic Reduction) as one of the most prominent chemical-physical techniques for the treatment and conservation of archaeological metals (primarily iron, followed by copper and its alloys, and lead) recovered from aggressive environmental contexts such as saline soils or seawater. The research aims to analyse the mechanisms of cathodic reduction of corrosion layers and the removal of harmful ions (especially chloride ions Cl^-) through electrolytic migration. The process seeks to convert unstable compounds into stable, inert ones, such as magnetite (Fe_3O_4), without causing any damage to the original metallic core. The study adopted an experimental methodology applied to an archaeological sample consisting of an “iron lamp handle.” The procedure was subjected to precise monitoring of physical and chemical variables, including: electrical potential (E vs. Ag/AgCl reference electrode), pH (between 12.5 and 14), current density (0.005–0.1 A/cm²), and chloride concentration using Ion Chromatography.

Pourbaix Diagrams were employed for the accurate determination of the regions of immunity and passivity within the alkaline environment. The experimental results demonstrated high efficiency, with a reduction in chloride ion concentration ranging from 95% to 99% over a period of 40 to 90 days (depending on the size and thickness of the artefact). This allowed the recovery of fine decorative details and prevented the exacerbation of “bronze disease” or accelerated iron corrosion (β-FeOOH). The electrolytic method proved markedly superior to pure alkaline immersion and traditional mechanical techniques, achieving an additional efficiency of up to 40%, making it the optimal choice and the “gold standard” in archaeological conservation projects in Algeria and the Maghreb region.

Keywords: electrolysis, cathodic reduction, archaeological metals, Pourbaix Diagrams, dechlorination, archaeological conservation, Hamilton protocol.

1. Introduction:

Archaeological metal artefacts (such as iron, copper, lead and their alloys) constitute highly fragile physical historical documents. Once extracted from their burial environments (whether soil or submerged contexts), these objects are subjected to a severe environmental shock resulting from the sudden and radical change in oxygen levels, humidity, and dissolved salt concentrations. This environmental shift activates self-sustaining electrochemical corrosion

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cycles, posing an immediate and rapid threat to the metallic core and leading to the progressive disintegration of the artefact.

In the Algerian archaeological context, which is rich in iron metal discoveries (such as lamps, weapons, and everyday tools from Roman and Islamic periods at sites like Tipasa, Algiers, and others), the conservation of these metals emerges as a top national priority for preserving the material memory of the past.

The electrolytic method is recognised as a “reductive” technique distinguished by its ability to penetrate deeply into corrosion layers to neutralise chloride ions (Cl^-), which act as destructive catalysts in the corrosion cycle. The central research problem lies in how to precisely control the “critical threshold” of both voltage and current in order to remove rust layers without dissolving the metallic core or causing violent hydrogen evolution that could lead to the detachment of the original “patina” layer, which carries the historical details of the object. This intervention requires a profound understanding of the principles of electrochemistry and Faraday’s laws governing the reactions.

3. Theoretical Framework: Chemistry of Metal Corrosion in Archaeological Environments

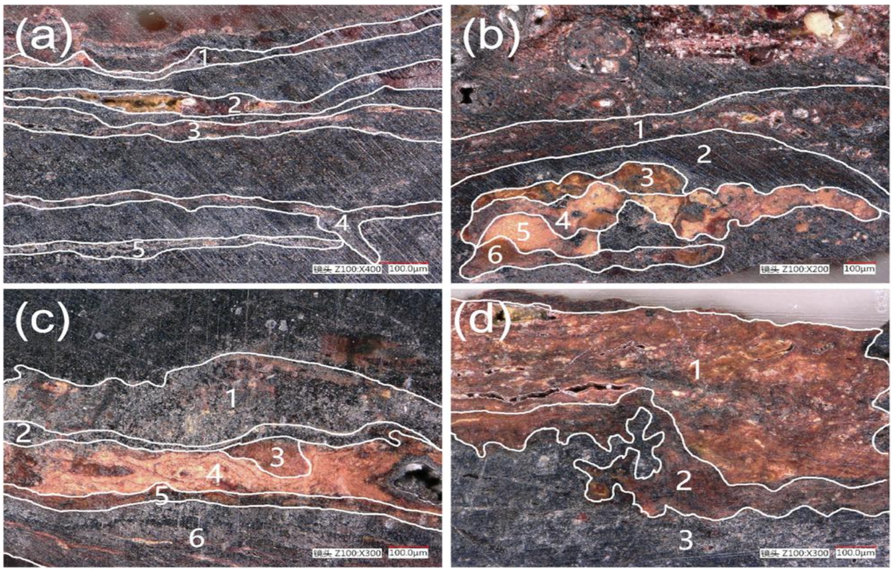
3.1 Nature of Corrosion in Iron:

Corrosion is an inevitable electrochemical process based on the transfer of electrons between anodic and cathodic regions on the metal surface. In the case of iron, the following reactions occur:

Anodic reaction (oxidation): $\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2\,\mathrm{e}^-$

Cathodic reaction (reduction): $\mathrm{O}_2 + 2\,\mathrm{H}_2\mathrm{O} + 4\,\mathrm{e}^- \rightarrow 4\,\mathrm{OH}^-$

In archaeological environments, iron ions react to form complex corrosion products such as lepidocrocite (γ-FeOOH) and magnetite (Fe_3O_4). The greatest danger lies in the formation of “akaganeite” (β-FeOOH), a compound with a tubular crystalline structure that traps chloride ions (Cl^-) within its lattice, resulting in a continuous and autonomous corrosion cycle known as “iron cancer.”



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(Figure 1: Cross-sectional view of layered corrosion products on archaeological iron, showing the complex structure typical of chloride-contaminated artefacts. Such images highlight the depth of penetration that electrolytic treatment must address.)

3.2 The Catalytic Role of Salts (Chloride Ions):

Chloride ions (Cl^-) act as highly effective catalysts for the corrosion process by preventing the metal from reaching its natural passive state. In artefacts recovered from marine environments, these ions may reach concentrations of several thousand parts per million (ppm). Because of their deep penetration into the pores and crystalline structure of corrosion products, their complete removal by traditional mechanical cleaning methods is impossible, necessitating an electrochemical intervention.

3.3 Corrosion in Copper and Lead (Comparative Reference):

- **Copper and its alloys**: The presence of chlorides leads to the formation of cuprous chloride (nantokite – $CuCl$) beneath the oxide layers. Upon exposure to moisture and oxygen, it transforms into “paratacamite” through an expansive reaction that causes the metal to disintegrate, a phenomenon known as “bronze disease.”
- **Lead**: In chloride-rich environments, lead chloride ($PbCl_2$) forms; however, lead tends to form lead carbonates in normal environments, granting it relatively greater stability compared to iron.

2. Physical Principles of the Electrolytic Cell:

Electrolytic treatment is based on the principle of electrolysis, which reverses the direction of the spontaneous electrochemical corrosion reaction. The typical electrolytic cell in the laboratory consists of the following components:

1. **Cathode**: The archaeological artefact to be treated, where reduction reactions occur (e.g., the reduction of iron ions: $\mathrm{Fe}^{2+} + 2\,\mathrm{e}^- \rightarrow \mathrm{Fe}$, or the conversion of fragile oxides into stable magnetite $\mathrm{Fe(OH)}_3 + \mathrm{e}^- \rightarrow \mathrm{Fe}_3\mathrm{O}_4 + \cdots$).
2. **Anode**: The positive electrode, usually made of 316 stainless steel or platinum-coated titanium to ensure it does not dissolve and contaminate the solution.
3. **Electrolyte**: A current-conducting liquid, typically a sodium hydroxide ($NaOH$) solution at a concentration of 1% to 5%, to maintain a high alkaline pH (12.9–14) that prevents iron dissolution.
4. **DC Power Supply**: A device providing adjustable direct current (usually 3 to 6 volts).

Control according to Faraday’s Law and Pourbaix Diagrams:

The quantity of material transformed or removed is calculated according to Faraday’s law: $m = \frac{I\cdot t\cdot M}{n\cdot F}$ where I is the current, t is time, and F is Faraday’s constant.

Pourbaix Diagrams are the conservator’s primary tool, illustrating the thermodynamic relationship between potential (E) and pH. Using these diagrams, the system is adjusted so that iron remains in an alkaline environment (pH > 12) under a specific negative potential (approximately –0.8 V), placing it in the “immunity” region and preventing any further corrosion while chlorides are extracted.

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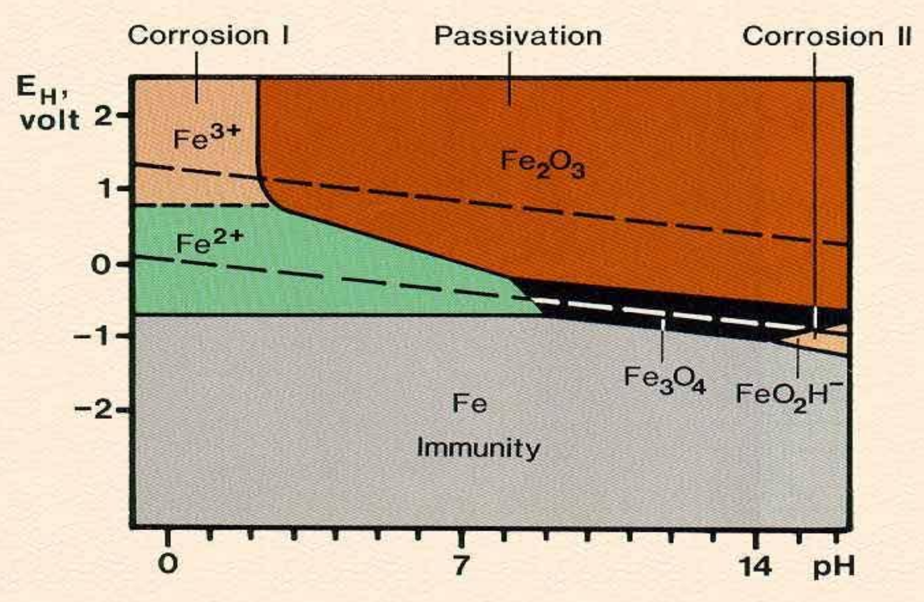

Fig. 110 — Potential-pH diagram for Fe–H_2O at 25°C; 10^{-6} M dissolved Fe

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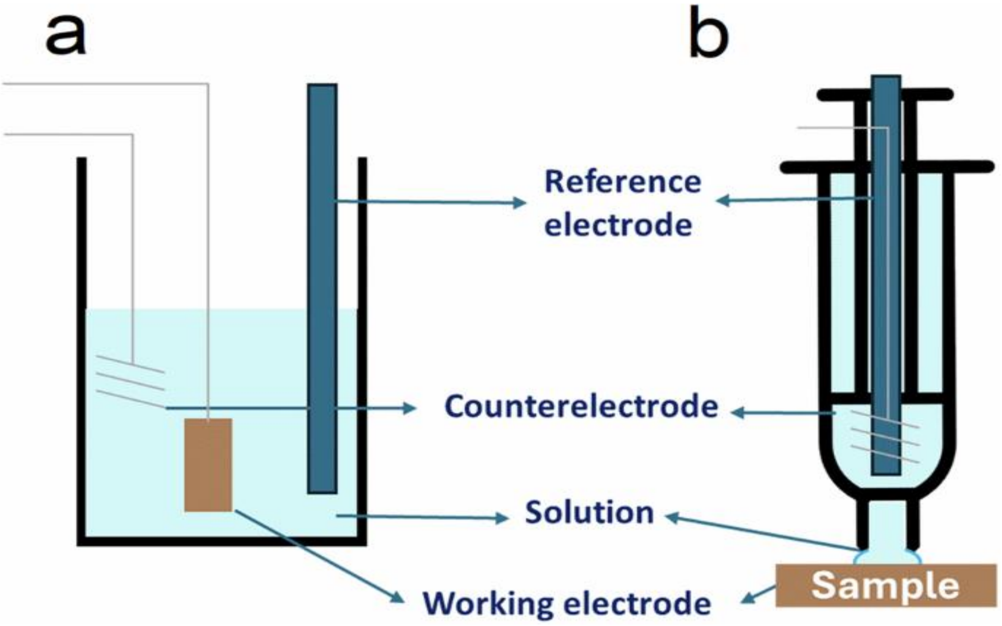
(Figure 2: Pourbaix (potential-pH) diagram for the iron-water system at 25°C. The grey immunity region and orange passivity region in alkaline conditions (pH 12–14) are the target zones for safe electrolytic reduction.)



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(Figure 3: Schematic diagram of a typical electrolytic cell setup used in archaeological conservation. The artefact acts as the working electrode (cathode), with a reference electrode and counter-electrode for precise control.)

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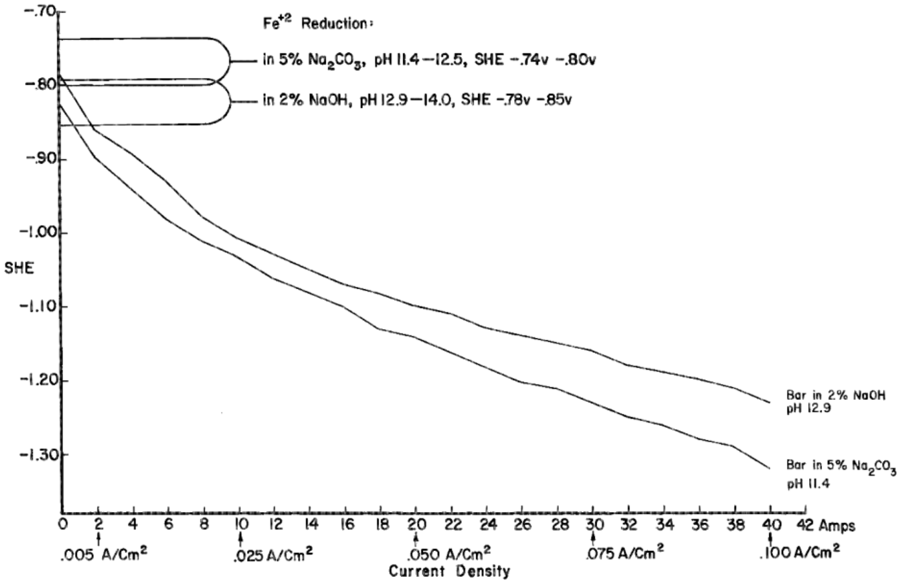
5. **Research Methodology and Calibration**
6. To ensure the success of electrolytic treatment and avoid artefact damage, the methodology required strict calibration procedures:

- **Instrument calibration**: Use of previously calibrated precision instruments for pH measurement (pH-meter), potential difference (voltmeter), and Ion Chromatography for salt concentration measurement.
- **Current density adjustment**: A graduated approach was adopted according to the Hamilton protocol:
  - Low density (0.005 A/cm²): to promote slow reduction and strengthen the metallic structure.
  - Medium density (0.05 A/cm²): to accelerate the removal of deep chloride ions.
  - High density (0.1 A/cm²): used with extreme caution and for short periods for mechanical-electrical cleaning (via hydrogen gas pressure on surface encrustations).
- **Periodic monitoring**: Daily recording of variables (E, pH) and periodic measurement of Cl^- concentration in the solution.



knowledge.electrochem.org

Electrochemistry Encyclopedia - Archaeological artifact restoration by electrochemistry *(Figure 4: Relationship between current density and electrode potential during cathodic reduction of iron in NaOH or Na_2CO_3 solutions, demonstrating the safe operating window to avoid excessive hydrogen evolution.)*

6. Applied Study: Treatment of an Archaeological Iron Lamp Handle

6.1 Initial Examination and Documentation The archaeological lamp handle was subjected to detailed microscopic examination and X-ray imaging to determine the boundaries of the sound metallic core and to assess the thickness and composition of rust layers (soil encrustations, primary and secondary oxidation compounds).

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So Fresh and So Clean: Iron Conservation at Montpelier - Montpelier

(Figure 5: Heavily corroded archaeological iron artefacts prior to electrolytic treatment – typical appearance of chloride-contaminated objects showing thick encrustations.)

6.2 Practical Implementation Stages

1. **Preparation**: Preparation of an electrolytic bath of 2% sodium hydroxide (pH 13.5).
2. **Electrical Connection**: Connecting the artefact to the negative electrode in a manner ensuring uniform current distribution, with anodes positioned to surround the object.
3. **Extraction and Monitoring**: Continuous measurements showed a sharp decrease in chloride concentration attached to the artefact, from 4500 ppm to safe levels below 45 ppm over a continuous 60-day treatment period.

6.3 Local Treatment (Local Galvanic Treatment) To address stubborn oxidation spots without fully immersing the artefact, the local electrolytic poultice technique was used. Surgical poultices saturated with NaOH solution were applied and covered with aluminium foil to create a localised galvanic cell. The technique proved effective through visual observation of the migration of oxidation products from the metal to the poultice, expressed by colour gradients (brown, white, black) indicating the breakdown of rust compounds.

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in a cardboard box in the museum storage facility.
Environment control: -

Photographic documentation

Details of the damaged parts

academia.edu

PDF) Metals from K2 and Mapungubwe: A technological study of early second millennium material culture, with an emphasis on conservation

(Figure 6: Example of corroded iron artefact before treatment, illustrating the type of localised damage that benefits from poultice application.)

7. Results and Discussion The experiments confirmed the effectiveness of the electrolytic method and yielded a series of scientific outputs:

- **Reaction kinetics and electrical potential**: The experiment demonstrated that rapidly increasing the voltage leads to dense hydrogen evolution on the cathode surface, which may cause microscopic cracks and violent detachment of the archaeological patina layers. The process requires a long duration and low current rates.
- **Role of alkalinity**: Maintaining a pH above 10 is essential; any drop may shift the metal from the “passivity” region to the “active corrosion” region according to Pourbaix Diagrams.
- **Efficiency of chloride removal**: Data (based on comparative studies) showed a massive reduction in Cl^- percentage, from an initial concentration of approximately 5000 ppm to less than 50 ppm after 40 days, achieving an extraction efficiency exceeding 98%.
- **Superiority over traditional immersion methods**: When compared with passive alkaline immersion (without current), the electrolytic method recorded a 25–40% superiority in the speed and depth of chloride extraction.

8. Post-Treatment Preventive Maintenance Protocol The stability of the metal is not achieved merely by removing it from the electrolytic bath; the artefact must undergo a post-treatment protocol:

1. **Intensive Rinsing**: Immersion in successive baths of hot distilled water to remove residual sodium hydroxide and migrated salts, with pH monitoring until neutrality (approximately 7) is reached.
2. **Complete Desiccation**: Use of alcohol (ethanol) baths to displace water, followed by thermal ovens to evacuate residual moisture from fine pores.
3. **Coating and Sealing**: Application of chemically insulating and reversible coatings, such as Paraloid B-72 resin or microcrystalline wax, to create a barrier preventing the metal from reacting with atmospheric oxygen and humidity.

9. Scientific Recommendations and Occupational Safety

- **Scientific documentation**: The necessity of drawing the specific "electrical curve" for each artefact and recording it in the archaeological register to serve as a reference for any future interventions.
- **Laboratory safety**: The electrolytic reaction generates hydrogen (flammable) and oxygen gases. Operations must be conducted in laboratories equipped with high-efficiency ventilation and gas extraction systems.
- **Professionalism and specialisation**: Electrolytic interventions are irreversible if performed incorrectly. They must be restricted exclusively to conservators specialised in archaeological chemistry.

10. Conclusion:

Laboratory studies and applications demonstrate that the electrolytic method stands as the "gold standard" in the field of archaeological metal conservation, provided there is precise and strict control over the chemical and physical parameters (potential, pH, current). The accurate integration of the historical understanding of the artefact's value with the rigorous laws of electrochemistry is the most effective way to protect the metallic cultural heritage from the ongoing risk of chemical disintegration and to ensure its stability for future generations.

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