

Article

Mild Chemical Cleaning of Corroded Bronze Using an APP-Based Composite Solution: Improved Post-Cleaning Corrosion Behaviour and Mechanistic Interpretation

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Abstract

The corrosion of copper alloys in buried or atmospheric environments is driven by the anodic dissolution of the copper matrix, a chloride-mediated autocatalytic cycle, and the accumulation of insoluble corrosion products, among which basic copper chlorides such as paratacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) are characteristic phases closely associated with the accelerated degradation of bronze artefacts. Here, we report a ternary aqueous cleaning system comprising ammonium polyphosphate (APP), boric acid, and the nonionic surfactant OP-10 for the removal of chlorine-containing corrosion products from simulated bronze substrates. Single-factor optimization identified the selected formulation of 4 wt% APP, 4 wt% boric acid, and 0.5 vol% OP-10, achieving an apparent corrosion-product removal efficiency of $93.7\% \pm 0.6\%$ with a total colour difference (ΔE^*) below 5. X-ray diffraction (XRD) and scanning electron microscopy (SEM) confirmed the effective removal of the loose, chlorine-rich outer corrosion layer while preserving the compact inner layer. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements showed that the charge transfer resistance (R_{ct}) increased and the corrosion current density (I_{corr}) decreased after cleaning, indicating an improvement in the short-term corrosion behaviour of the surface, which may be associated with the removal of chloride-bearing phases and/or the residual compact Cu_2O layer, with a possible contribution of the adsorption of residual phosphate species on the substrate. This study provides a simple chemical route for the mild cleaning of corroded bronze surfaces and offers a preliminary exploration of polyphosphate-based systems for the conservation of copper-based cultural heritage.

Keywords: copper alloy; corrosion products; ammonium polyphosphate; chemical cleaning; bronze conservation; chloride removal



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1. Introduction

Copper and its alloys have been widely used in historical, artistic, and industrial fields, among which bronze (Cu–Sn–Pb alloy) is one of the most important engineering materials in antiquity. Among bronze artefacts, ancient coins constitute a unique category, providing

valuable information for the study of ancient metallurgical technology, economic systems, and social development [1–5]. However, owing to prolonged circulation and burial, most copper coins have suffered varying degrees of corrosion, which alters their original appearance, obscures inscriptions, and damages the metal substrate [6–10]. Therefore, developing effective methods for removing corrosion products that preserve the morphology, inscriptions, and substrate integrity is of considerable theoretical and practical significance for the conservation and study of copper coins [11]. Existing approaches for removing corrosion products from bronze include mechanical, laser and chemical cleaning [7,12]. Mechanical cleaning is operator-dependent and may scratch fine inscriptions [7], whereas laser cleaning is costly and of limited applicability to thin-walled, intricately decorated objects such as coins [13,14]. Chemical cleaning offers high efficiency and uniform treatment but may cause over-corrosion of the substrate if not properly controlled [15–18]. Given the small size, thin walls, and densely packed inscriptions of bronze coins, the cleaning process imposes stringent requirements in terms of selectivity and safety [19,20].

In conservation practice, the established chemical treatments for chloride-bearing corrosion on copper alloys include aqueous sodium sesquicarbonate ($\text{Na}_2\text{CO}_3/\text{NaHCO}_3$) baths, alkaline dithionite reduction, Rochelle salt, benzotriazole, and carbonate-based baths, which constitute the operational standard in restoration laboratories [17,21–23]. The benchmark study of MacLeod [17] quantitatively compared several dechlorination methods for corroded copper alloys and remains the standard reference for evaluating chloride-removal efficiency. Chelator-based chemical systems can form water-soluble complexes with metal ions under relatively mild conditions, thereby promoting the dissolution of corrosion products [24–26]. More recently, confined hydrogels and nanofluids, enzymatic and biological systems, and ionic liquids have been proposed as advanced cleaning media for cultural heritage surfaces [27–30]. In a different field, polyphosphates are well-established copper corrosion inhibitors in drinking-water distribution systems [31,32]; the present work therefore transfers a chemically known interaction into a conservation context rather than claiming new coordination chemistry.

Here we report a ternary aqueous cleaning system comprising ammonium polyphosphate (APP), boric acid, and the nonionic surfactant OP-10 (octylphenol polyoxyethylene ether), designed for the simultaneous removal of chlorine-containing corrosion products and improvement of the post-cleaning corrosion behaviour of simulated bronze substrates. In this system, APP is the core active component: upon dissolution and partial hydrolysis, it generates phosphate species, chiefly pyrophosphate and oligomeric polyphosphate anions, that form water-soluble complexes with Cu^{2+} , continuously withdrawing dissolved copper ions from the reaction interface and thereby driving the sustained dissolution of the corrosion products. Boric acid (H_3BO_3) lowers and helps modulate the pH of the working solution toward the near-neutral range (measured pH ≈ 6.9 for the selected formulation), while OP-10 reduces the interfacial tension between the solution and the porous corrosion layer, enhancing wetting and inward penetration of the active components. The formulation was selected by single-factor experiments, and the treated surfaces were characterized by SEM-EDS and XRD to evaluate phase composition and microstructural evolution; potentiodynamic polarization and EIS measurements were employed to assess the short-term post-cleaning corrosion behaviour [33]. In the electrochemical tests, the cleaned surfaces exhibited improved corrosion behaviour relative to the corroded state, which may arise from the removal of active chlorine-containing phases and/or the residual compact Cu_2O layer, with a possible contribution of residual phosphate species. From the viewpoint of conservation ethics, any treatment of an artefact should respect the principles of minimum intervention, recognizability, reversibility, and the protection of the noble patina and the original surface [34,35]; a cleaning formulation that removes the outer corrosion layer

and may leave a residual phosphate-containing layer constitutes a permanent chemical modification of the artefact surface, and its application must therefore be justified by the conservation objectives, rather than by removal efficiency alone. This work demonstrates the potential of polyphosphate-based systems for the mild cleaning of corroded bronze on simulated specimens, offering a practical route for the conservation of copper-based cultural heritage.

2. Materials and Methods

2.1. Materials

2.1.1. Specimen Preparation

Commercially available imitation ancient copper coins were used as simulated bronze substrates. Each specimen was a round coin with a central square hole, with a diameter of 20.0 mm, a thickness of 1.5 mm, and a central square hole side length of 5.0 mm, giving a total geometric surface area of approximately 7.0 cm². The imitation coins were cast from a Cu–Sn–Pb ternary alloy. The elemental composition was verified by X-ray fluorescence (XRF), yielding measured mass fractions of $74.2 \pm 1.1\%$ Cu, $9.8 \pm 0.6\%$ Sn, and $16.0 \pm 0.9\%$ Pb. The imitation coins were purchased from Yuanxing Metal Co., Ltd., China. The absence of manufacturer-applied patination or protective coating on the specimen surface was confirmed by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) and X-ray diffraction (XRD) prior to corrosion treatment. The use of imitation specimens, which is common practice in conservation research, ensures experimental reproducibility while avoiding potential damage to genuine cultural relics [36–38].

2.1.2. Chemical Reagents

All reagents used for artificial corrosion were of analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), including sodium chloride (NaCl, $\geq 99.5\%$), sodium sulfate (Na₂SO₄, $\geq 98\%$), and sodium bicarbonate (NaHCO₃, $\geq 99.8\%$).

Reagents used in the cleaning system included ammonium polyphosphate (APP, analytical grade), boric acid (H₃BO₃, analytical grade, $\geq 99.5\%$), and OP-10 (octylphenol polyoxyethylene ether, purity 99.9%). APP was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. According to the supplier's label, the declared degree of polymerization of the APP is $n \leq 20$; X-ray diffraction (XRD) confirmed its short-chain structure (crystalline form I), and the product was fully soluble in deionized water: a 4 wt% aqueous solution was clear and transparent with no visible insoluble residue, and centrifugation showed no obvious stratification (the supplier's Certificate of Analysis, XRD analysis, dissolution test, and centrifugation test are detailed in the Supplementary Materials). All experiments reported in this work, were performed with this APP product (Shanghai Macklin, $n \leq 20$). Boric acid was purchased from Anhui Zesheng Technology Co., Ltd., and OP-10 from Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium chloride (NaCl, analytical grade, $\geq 99.5\%$) used for the electrochemical tests was purchased from Sinopharm Chemical Reagent Co., Ltd. Silver nitrate standard solution (AgNO₃, 0.01 mol/L, commercially standardized) and concentrated nitric acid (HNO₃, analytical grade), used for the potentiometric chloride titration, were purchased from Shengshi Biaowu (Xiamen) Technology Co., Ltd. (Xiamen, China) and Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), respectively. All reagents were used as received without further purification. Deionized water was used throughout the experiments.

2.2. Methods

2.2.1. Specimen Preparation and Corrosion Procedure

To obtain a stable and reproducible initial state, all specimens were sequentially polished with silicon carbide abrasive papers (400, 800, and 1200 grit), ultrasonically cleaned in acetone for 5 min to remove surface grease and contaminants, rinsed with deionized water, and dried under a nitrogen stream. The specimens were then weighed to record their initial mass (m_0) and stored in a desiccator until use. These pretreated specimens were designated as Phase I samples.

The corrosion solution was composed of 0.5 mol/L NaCl and 0.1 mol/L Na₂SO₄, with 0.05 mol/L NaHCO₃ added to adjust the pH to 8.5–9.0. The solution volume-to-specimen surface area ratio was maintained at 20 mL/cm², and the corrosion solution was renewed every 48 h to avoid depletion of reactive species and accumulation of dissolved corrosion products. An alternating wet–dry cycle was applied for 14 days at 30 °C and 85% relative humidity: each cycle consisted of 12 h of full immersion in the corrosion solution followed by 12 h of air-drying under controlled temperature and humidity conditions. The 14-day corrosion duration was selected based on pre-experimental monitoring: the mass gain of the specimens reached a plateau after approximately 12 days, and X-ray diffraction (XRD) confirmed the formation of nantokite (CuCl) and paratacamite (Cu₂(OH)₃Cl)—the two phases most relevant to bronze disease—after 14 days of cycling.

After the corrosion treatment, the specimens were gently rinsed with deionized water to remove loosely adherent soluble salts, naturally dried at room temperature, and stored in a desiccator until use. These corroded specimens were designated as Phase II samples.

2.2.2. Cleaning Treatment

The composite cleaning solution was prepared according to the selected formulation ratio. APP and boric acid were sequentially added to deionized water to prepare 100 mL of the solution and magnetically stirred at 30 °C until completely dissolved. OP-10 was then added dropwise, and stirring was continued for an additional 10 min until a homogeneous and transparent solution was obtained. The prepared cleaning solution was preheated in a 30 °C water bath for 10 min, after which the Phase II (corrosion-treated) samples were fully immersed in the solution. The cleaning solution was freshly prepared and used immediately for each batch of specimens; storage of the prepared solution was avoided because the slow hydrolysis of the short-chain APP slightly lowers the pH over time, which could affect the reproducibility of the treatment. All cleaning experiments were performed with freshly prepared working solutions at a measured pH of ≈ 6.9 (Section 3.2.2).

The cleaning process employed ultrasonic assistance to promote the detachment and dissolution of the corrosion layer. Ultrasonic treatment was performed using a KQ-50DE bath-type ultrasonicator (Kunshan Ultrasonic Instruments Co., Ltd., China) operating at a frequency of 40 kHz and a power of 120 W. The specimens were fully immersed in the cleaning solution and placed at the center of the ultrasonic bath. Each ultrasonic cycle consisted of 3 min of sonication at 30 °C, followed by a 7 min standing interval; this cycle was repeated three times. The total treatment duration was 30 min, comprising 9 min of effective sonication time and 21 min of standing intervals. Three parallel specimens were used for each formulation in the optimization experiments. It should be noted that ultrasonic cavitation may be destructive to fragile patinas or mineralized inscriptions on delicate artefacts. In the present work, the ultrasound was applied at a low power (120 W), and the protocol was developed for robust imitation coins; its application to more fragile objects therefore requires appropriate caution.

After cleaning, the samples were sequentially rinsed three times with deionized water and anhydrous ethanol, dried under a nitrogen stream at room temperature, and then

subjected to characterization and electrochemical tests. These specimens were designated as Phase III samples. The experimental procedure is shown in Figure 1.

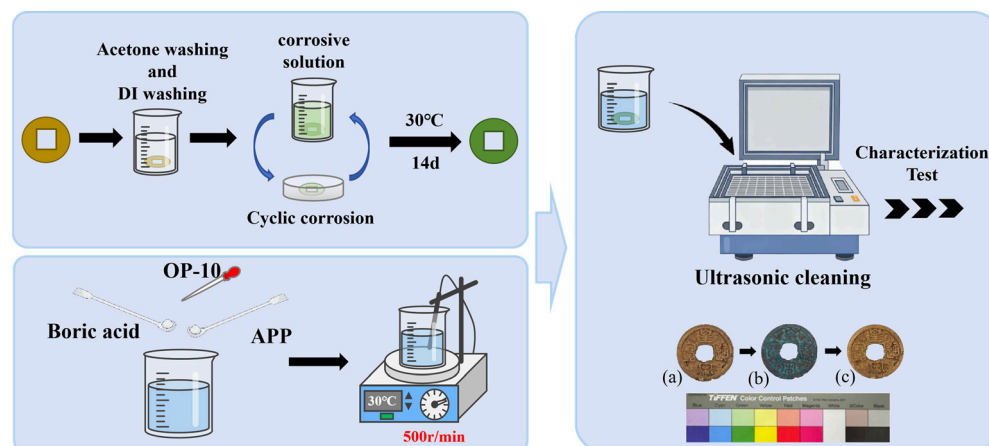


Figure 1. Process Flow Diagram. (a) Phase I—as-cast bronze substrate; (b) Phase II—artificially corroded bronze; (c) Phase III—after cleaning treatment.

2.2.3. Surface Morphology and Elemental Analysis

The elemental composition of the sample surfaces before and after cleaning was assessed by two complementary techniques. X-ray fluorescence (XRF; XRF-1800, Shimadzu, Japan) probes a surface region of the order of micrometres and provides semi-quantitative compositional information integrated over the analysed area, whereas scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS; SU8020, Hitachi, Japan, with an attached EDS detector) provides local point and mapping information at higher lateral resolution but from a smaller sampling volume. These techniques are therefore complementary and are reported as such rather than as interchangeable. Phase characterization was performed with an XRD-D8 DISCOVER A25 X-ray diffractometer (Bruker, Germany), and the surface morphology was observed with the SU8020 field emission SEM.

2.2.4. Corrosion Product Removal Efficiency

The corrosion product removal efficiency was evaluated by measuring the sample mass before and after cleaning, and calculated according to Equation (1):

$$\eta = \frac{m_1 - m_2}{m_1 - m_0} \times 100\% \quad (1)$$

where η is the corrosion product removal efficiency (%); m_0 is the mass of the Phase I sample (original uncorroded sample); m_1 is the mass of the Phase II sample (after artificial corrosion, before cleaning); and m_2 is the mass of the Phase III sample (after cleaning).

It should be noted that this gravimetric formula assumes that the mass gain ($m_1 - m_0$) solely represents corrosion products and that the mass loss ($m_1 - m_2$) solely represents removed corrosion products. In practice, partial dissolution of the copper substrate during the 14-day corrosion cycle and slight substrate attack during cleaning may introduce a systematic offset in the apparent removal efficiency. Therefore, the reported η values should be interpreted as apparent removal efficiencies, and the relative trends across formulation groups are considered more reliable than the absolute values.

2.2.5. Colour Difference Analysis

An X-Rite VS450 non-contact benchtop spectrophotometer (X-Rite Inc., USA) was used to evaluate the colour changes in the sample surfaces before and after cleaning. The instru-

ment employs a $45^\circ/0^\circ$ measurement geometry (dual 45° illumination, 0° detection; specular component excluded), a measurement aperture of 6 mm, and an illuminant/observer combination of D65/ 10° . Three measurement locations per specimen were averaged. Using the surface chromaticity parameters of the Phase I sample (original uncorroded sample) as the reference, the Phase III (cleaned) samples were tested, and the total colour difference (ΔE^*) was calculated according to Equation (2) in the CIELAB 1976 colour space. In this context, ΔE^* referenced to Phase I quantifies the completeness of cleaning, i.e., how closely the surface approaches the bare metal, and should not be interpreted as an index of chromatic damage induced by the cleaning process.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

where ΔL^* , Δa^* , and Δb^* represent the differences in lightness, red–green chromaticity, and yellow–blue chromaticity between the Phase I and Phase III specimens, respectively. We note that the $\Delta E^* < 5$ criterion adopted here is more lenient than the $\Delta E^* < 3$ threshold commonly used in conservation practice [39], i.e., the colour change in the cleaned surface is considered acceptable in this work.

2.2.6. Potentiometric Determination of Chloride Released into the Cleaning Solution

To quantitatively evaluate the removal of chloride-bearing corrosion products, the chloride content of the working solution after the standard cleaning treatment was determined by potentiometric titration. A 5.00 mL aliquot of the treated working solution was transferred to a 25 mL volumetric flask, diluted to the mark with deionized water, and acidified with concentrated nitric acid (analytical grade) to $\text{pH} < 2$ to avoid the precipitation of silver oxide and the interference of phosphate species with the titration. The entire diluted solution was then titrated with a standardized 0.01 mol/L AgNO_3 solution under continuous stirring, using a silver wire as the indicator electrode and a saturated calomel electrode (SCE) as the reference electrode. The cell potential was recorded as a function of the titrant volume (open-circuit potential–time mode of the CHI760E workstation), and the equivalence point was identified from the maximum of the first derivative of the titration curve. A blank titration was performed with an equal volume of deionized water subjected to the same procedure, and each measurement was carried out in triplicate. The chloride concentration was calculated using Equation (3).

$$C(\text{Cl}^-) = (V - V_0) \times c(\text{AgNO}_3) \times M(\text{Cl})/V_{\text{al}} \times 1000 \quad (3)$$

where V and V_0 are the titrant volumes for the sample and the blank (mL), respectively, $c(\text{AgNO}_3)$ is the concentration of the standard AgNO_3 solution (0.01 mol/L), $M(\text{Cl})$ is the molar mass of chlorine (35.45 g mol^{-1}), and V_{al} is the volume of the aliquot (5.00 mL). The measured chloride concentration in the working solution after the standard 30 min treatment was $203 \pm 4 \text{ mg/L}$ ($n = 3$).

2.2.7. Electrochemical Measurements

Electrochemical tests were performed using a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). A standard three-electrode system was employed, with the coin specimen as the working electrode (coated with Kafuter silicone sealant to expose an area of 1.0 cm^2), a platinum electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte was a 3.5 wt% NaCl solution, and the temperature was maintained at $30 \pm 2^\circ \text{C}$. To avoid the polarization scan modifying the specimen surface examined by EIS, the electrochemical impedance spectroscopy (EIS) measurement was always performed before the polarization test on the

same specimen. The working electrode was immersed in the solution for approximately 1 h until a stable open-circuit potential was reached, and a sinusoidal perturbation signal with an amplitude of 5 mV was applied over a frequency range from 100 kHz to 0.1 Hz. The impedance data were fitted using ZView software. Tafel polarization measurements were conducted at a scan rate of 1 mV s^{-1} over a potential range of $E_{\text{ocp}} \pm 300 \text{ mV}$.

3. Results and Discussion

3.1. Microstructural Characterization of the As-Cast Bronze Substrate

Figure 2 shows the microstructural characteristics of the Phase I (original uncorroded) simulated bronze specimen. The metallographic image (Figure 2a) reveals a typical as-cast dendritic structure, which is a characteristic feature formed during the non-equilibrium solidification of copper alloys. The magnified image (Figure 2b) reveals a multiphase structure: the copper matrix appears as light regions, while the tin-rich phase is distributed in the interdendritic regions in the form of darker particles. SEM-EDS results (Figure 2c) indicate that copper is uniformly distributed as the primary matrix, while tin forms a solid solution with copper. Lead is dispersed in the alloy as a particulate second phase. These characteristics are consistent with the typical microstructure of leaded tin bronze (Cu–Sn–Pb) [40,41].

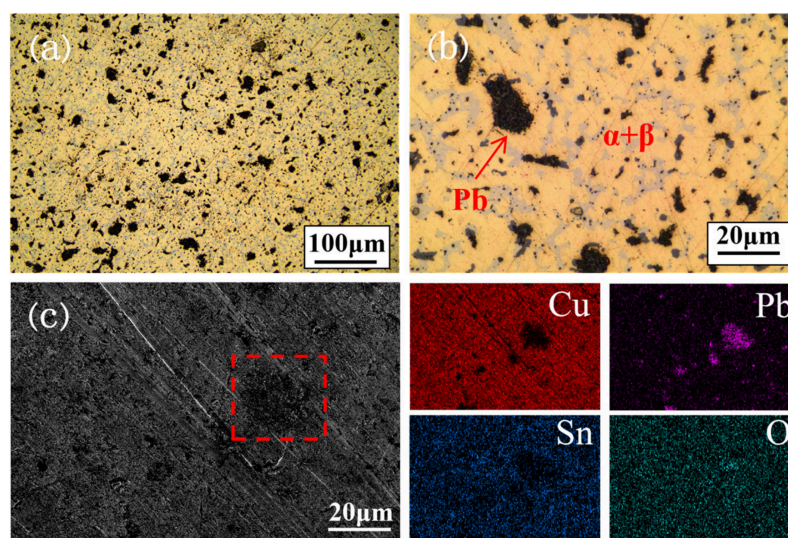


Figure 2. Analysis results of Phase I samples: (a,b) Metallographic microstructure; (c) SEM-EDS elemental mapping showing the distribution of Cu, Pb, Sn and O.

3.2. Optimization of the APP–Boric Acid–OP-10 Ternary Cleaning System

To ensure high corrosion product removal efficiency while minimizing reagent consumption and potential attack on the metal substrate, this study employed a single-factor variable method to systematically optimize the concentrations of the three components—APP, boric acid, and OP-10. The favorable addition amount of each component was selected by evaluating the apparent corrosion-product removal efficiency, surface morphology, and degree of substrate erosion under each formulation. It is acknowledged that single-factor optimization, in which each component is varied while the others are held at their previously selected levels, does not capture possible interactions among the three components; the resulting formulation should therefore be regarded as a favorable rather than a globally optimal composition. Partial deconvolution of the component contributions is provided by the control groups in Table 1 (Groups a-1, b-1, c-1, d and e).

Table 1. Optimization of the composite cleaning solution composition: effects of APP, boric acid, and OP-10 concentrations on the apparent corrosion-product removal efficiency.

Group	No.	APP (wt%)	Boric Acid (wt%)	OP-10 (vol%)	Sonication (120 W, 3 min × 3 Cycles)	Apparent Removal Efficiency (%)
a	a-1	-	4.0	0.5	✓	29 ± 2
	a-2	1.0	4.0	0.5	✓	47 ± 2
	a-3	2.0	4.0	0.5	✓	62 ± 2
	a-4	4.0	4.0	0.5	✓	94 ± 1
	a-5	8.0	4.0	0.5	✓	94 ± 1
	a-6	12.0	4.0	0.5	✓	91 ± 1
b	b-1	4.0	-	0.5	✓	66 ± 2
	b-2	4.0	1.0	0.5	✓	79 ± 2
	b-3	4.0	2.0	0.5	✓	81 ± 2
	b-4	4.0	4.0	0.5	✓	93 ± 1
	b-5	4.0	8.0	0.5	✓	93 ± 1
	b-6	4.0	10.0	0.5	✓	94 ± 1
c	c-1	4.0	4.0	-	✓	74 ± 2
	c-2	4.0	4.0	0.2	✓	87 ± 2
	c-3	4.0	4.0	0.5	✓	94 ± 1
	c-4	4.0	4.0	1.0	✓	96 ± 1
	c-5	4.0	4.0	2.0	✓	97 ± 1
	c-6	4.0	4.0	4.0	✓	94 ± 1
d	/	0	0	0	✓	16 ± 2
e	/	4.0	4.0	0.5	×	69 ± 2

Note: All efficiencies are apparent values. The same formulation (a-4, b-4 and c-3) giving 94%, 93% and 94%, i.e., 93.7% ± 0.6%; the differences among the 93%–97% values in the table are therefore within experimental variability. Values are the mean ± standard deviations (SD) of three parallel specimens. ✓ indicates that ultrasonic treatment (120 W, 3 min × 3 cycles) was applied, and × indicates that no ultrasonic treatment was applied.

3.2.1. Effect of APP Concentration on Cleaning Performance

APP serves as the primary complexing agent in the composite cleaning system. Its polyphosphate anions can form stable water-soluble complexes with Cu^{2+} through multiple coordination sites, thereby continuously removing dissolved copper ions from the reaction interface. To determine the favorable addition amount of APP, the effect of APP mass fraction on the corrosion product removal efficiency and the surface condition after cleaning was investigated with the concentrations of boric acid (4.0 wt%) and OP-10 (0.5 vol%). The experimental results are summarized in Table 1 (Group a). In the absence of APP (formulation a-1), the apparent removal efficiency was only 29%, indicating that boric acid and OP-10 alone were insufficient to remove the corrosion layer effectively. With a gradual increase in the APP mass fraction, the corrosion product removal efficiency (η) increased significantly. When the APP mass fraction reached or exceeded 4.0 wt%, the corrosion products could be effectively removed after 30 min of treatment. Further increasing the APP concentration resulted in only a limited improvement in removal performance. This phenomenon is attributed to the polyphosphate anions generated by the dissolution and hydrolysis of APP in aqueous solution, which can form stable complexes with the Cu^{2+} released during the dissolution of corrosion products, thereby driving the dissolution equilibrium forward and accelerating the removal of the corrosion layer. However, excessive APP may increase the viscosity of the solution and hinder diffusion, which could account for the slight decrease in apparent efficiency at 12 wt%; this explanation is a hypothesis and was not directly measured in the present work. The colour

change in the sample surfaces before and after treatment was further evaluated by colour difference analysis. Using the chromaticity data of the Phase I sample as the reference standard, colour difference analysis was performed on the treated samples. As shown in Figure 3a–d, the surface colour difference value (ΔE^*) gradually decreased with increasing APP mass fraction. When the APP mass fraction was ≥ 4.0 wt%, all ΔE^* values were below 5, indicating that the colour change was not significant. Therefore, the APP mass fraction was maintained at 4.0 wt% in subsequent experiments.

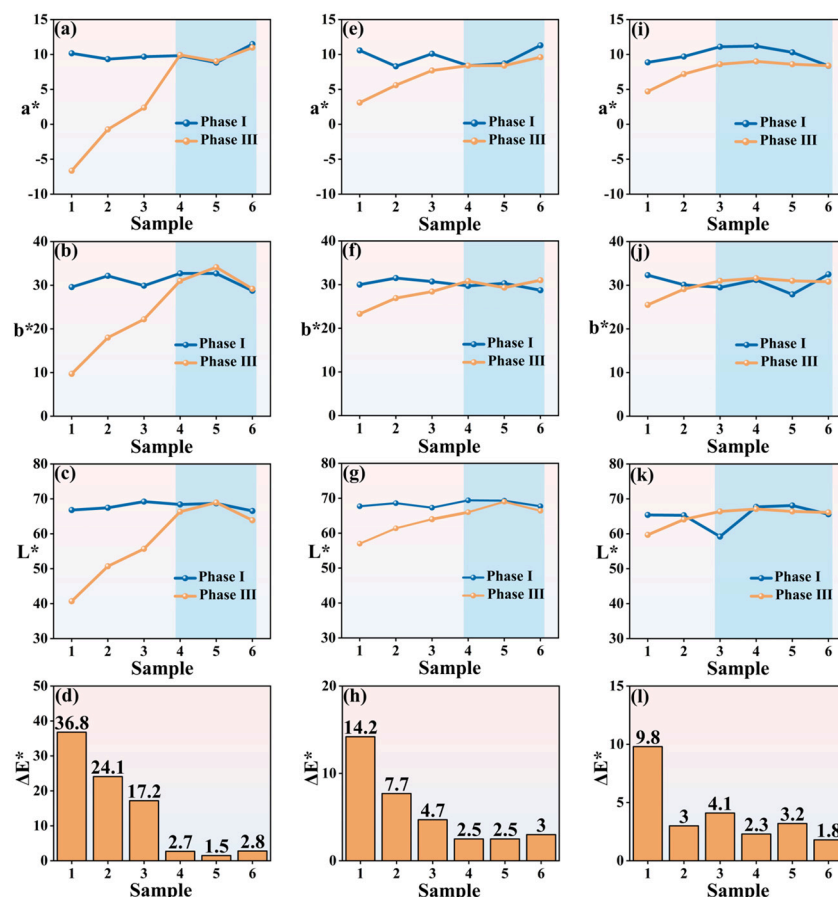


Figure 3. Comparison of colour differences between the Phase I sample and Phase III sample. (a–d) APP experimental group; (e–h) boric acid experimental group; (i–l) OP-10 experimental group.

3.2.2. Effect of Boric Acid Concentration on Cleaning Performance

After selecting the APP concentration (4.0 wt%), the effect of boric acid concentration on the cleaning performance was investigated while maintaining the OP-10 dosage at 0.5 vol%. The experimental results are summarized in Table 1 (Group b).

In the absence of boric acid, the apparent removal efficiency was only 66%, indicating that the cleaning capability of APP alone is limited. When the boric acid mass fraction was ≥ 4.0 wt%, the corrosion products could be effectively removed within 30 min, and the apparent removal efficiency stabilized above 90%. The pH of freshly prepared solutions was measured for each boric acid dosage. The pH decreased from 7.48 (0 wt% boric acid) to 6.06 (10 wt% boric acid), remaining near-neutral (pH 6.0–7.5) throughout the boric acid series; at the selected boric acid content (4 wt%), the pH was 6.88. Because boric acid (pK_a 9.24) is largely undissociated at $pH \approx 6.9$, its direct buffering contribution at the working pH is limited; the pH of the series is governed mainly by the phosphate buffer system derived from the hydrolysis of short-chain APP ($H_2PO_4^-/HPO_4^{2-}$, $pK_{a2} \approx 7.2$). The marked increase in removal efficiency upon boric acid addition (66% $\rightarrow$ 93%) therefore cannot be

attributed to the modest pH shift (≈ 0.6 pH units at 4 wt%); the underlying mechanism remains to be clarified and is discussed further in Section 4. Colour difference analysis (Figure 3e–h) demonstrated that when the boric acid content was ≥ 4.0 wt%, all ΔE^* values were below 5, indicating no significant colour change. In summary, the favorable mass fraction of boric acid was selected as 4.0 wt%; the small efficiency differences among the formulations with ≥ 4 wt% boric acid (93%–94%) are within the experimental variability of approximately $\pm 1\%$.

3.2.3. Effect of OP-10 Dosage on Cleaning Performance

With APP (4.0 wt%) and boric acid (4.0 wt%) held constant, the effect of the surfactant OP-10 was studied, and the experimental results are summarized in Table 1 (Group c). In the absence of OP-10, the apparent removal efficiency was only 74%, demonstrating that the surfactant contributes significantly to the cleaning process. As the OP-10 dosage increased, the removal efficiency improved markedly, and for volume fractions $\geq 0.5\%$, the corrosion products were effectively removed within 30 min, with apparent removal efficiencies exceeding 90%. However, at OP-10 volume fractions $\geq 2.0\%$, excessive foaming was observed during the cleaning process, which affected the stability and operational convenience of the process; this is attributed to the amphiphilic structure of OP-10, which readily stabilizes air bubbles in aqueous solution. Colour difference analysis (Figure 3i–l) showed that for OP-10 volume fractions $\geq 0.2\%$, all ΔE^* values remained below 5, indicating no significant colour change before and after treatment.

It is important to note that the same formulation (4 wt% APP, 4 wt% boric acid, 0.5 vol% OP-10) appears three times in Table 1 (Groups a-4, b-4 and c-3), giving apparent efficiencies of 94%, 93% and 94% ($93.7\% \pm 0.6\%$). The apparent efficiencies obtained for OP-10 dosages of 0.5–4 vol% (94%–97%) were similar in magnitude, with differences comparable to the experimental variability of approximately $\pm 1\%$; they were therefore considered operationally equivalent. Consequently, 0.5 vol% OP-10 was selected as an operationally favorable dosage rather than a statistically distinct performance optimum, because higher surfactant concentrations (≥ 2 vol%) caused excessive foaming.

Based on the above experimental results, the favorable formulation of the composite cleaning solution was selected as 4 wt% APP, 4 wt% boric acid and 0.5 vol% OP-10, achieving an apparent removal efficiency of $93.7\% \pm 0.6\%$ with a total colour difference (ΔE^*) below 5. This formulation provides high cleaning efficiency while limiting foaming and minimizing visible alteration of the specimen. To deconvolute the respective contributions of chemical dissolution and ultrasonic mechanical action to the overall cleaning performance, two control experiments were designed and conducted, as listed in Table 1 (Groups d and e). In the water + ultrasound-only group (group d), the apparent removal efficiency was only 16%, with only the loosely adherent surface powder detached and a residual colour difference of $\Delta E^* = 37.3$ relative to the Phase I reference, confirming that ultrasonic cavitation alone is insufficient to remove the bulk of the corrosion layer. In contrast, the selected formulation under static immersion (group e, without ultrasonication, 30 min) achieved an apparent removal efficiency of 69% with $\Delta E^* = 14.7$, demonstrating that chemical dissolution serves as the dominant cleaning mechanism. Collectively, these results indicate that the combined process arises from the synergistic action of chemical dissolution and ultrasonic assistance, where ultrasonication enhances mass transport across the solid–liquid interface and promotes the mechanical detachment of chemically loosened corrosion products. Figure 4 presents comparative photographs of the Phase II (corroded) and Phase III (cleaned) samples, providing direct visual evidence of the cleaning efficacy discussed above.

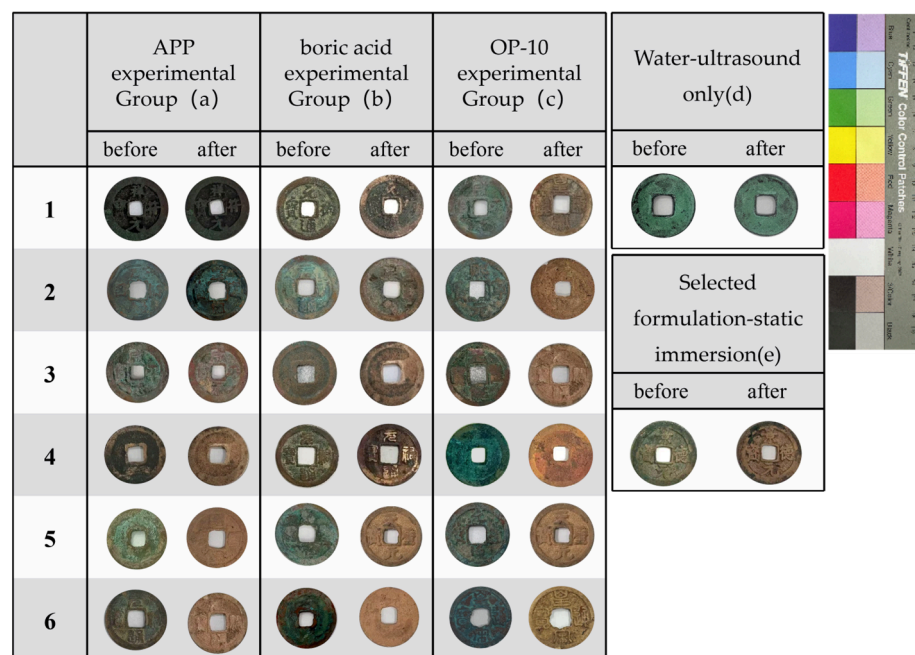


Figure 4. Visual comparison of bronze coin specimens from Phases II and III. Photographs were taken under natural daylight illumination, with the specimens placed on a white A4 paper background alongside a standard colour reference card.

3.2.4. Quantitative Assessment of Chloride Removal

To quantitatively evaluate the removal of chloride-bearing corrosion products, the chloride content of the working solution after the standard 30 min cleaning treatment was determined by potentiometric titration with standard AgNO_3 solution (Section 2.2.6). The measured chloride concentration was $203 \pm 4 \text{ mg/L}$ ($n = 3$), corresponding to approximately 20.3 mg of chloride removed per specimen ($\approx 2.9 \text{ mg cm}^{-2}$). This direct measurement confirms that chlorine-containing corrosion products are effectively removed from the specimen surface and transferred into the solution phase during cleaning. A quantitative benchmark against the dechlorination efficiencies reported for conventional treatments (e.g., alkaline immersion in the comparative study of MacLeod [17]) would require the chloride content of the corrosion layer before and after treatment on the same basis; such data are not available for the accelerated corrosion layers of the present simulated specimens, and an equal-terms comparison is therefore not possible. Accordingly, the gravimetric removal efficiency reported in Section 3.2.2 and the dechlorination efficiencies of other methods are deliberately not juxtaposed, because these quantities are not commensurable.

3.3. Surface Topography Analysis

To evaluate the cleaning effectiveness of the selected formulation, the surface morphology of the samples before and after treatment was characterized by scanning electron microscopy (SEM) (Figure 5). The untreated Phase II sample (corroded state) was covered with a loose corrosion layer that obscured the original morphology of the underlying substrate (Figure 5a). After cleaning with the selected formulation, the loose, lamellar corrosion products were effectively removed, exposing a relatively uniform surface (Figure 5b). Notably, micropores (approximately 2–10 μm in diameter) could be observed in Figure 5b; these are tentatively attributed to pre-existing casting defects and to pitting formed during the artificial corrosion process, although a contribution from microscopic substrate attack during cleaning cannot be fully excluded. The presence of these micropores suggests that the cleaning process preferentially removed the non-adherent outer corrosion products without causing macroscopic erosion damage to the metal substrate. Cross-sectional

SEM images (Figure 5c,d) further confirmed that the corrosion layer consisted of a loose, porous outer layer and a relatively compact inner layer; after treatment, the outer corrosion products were largely removed, and no obvious interfacial delamination or penetrating cracks were observed. EDS mapping analysis revealed that the O and Cl contents on the surface decreased significantly after cleaning, signifying the effective removal of active chlorine-containing corrosion phases, which is crucial for interrupting the corrosion cycle induced by chloride ions.

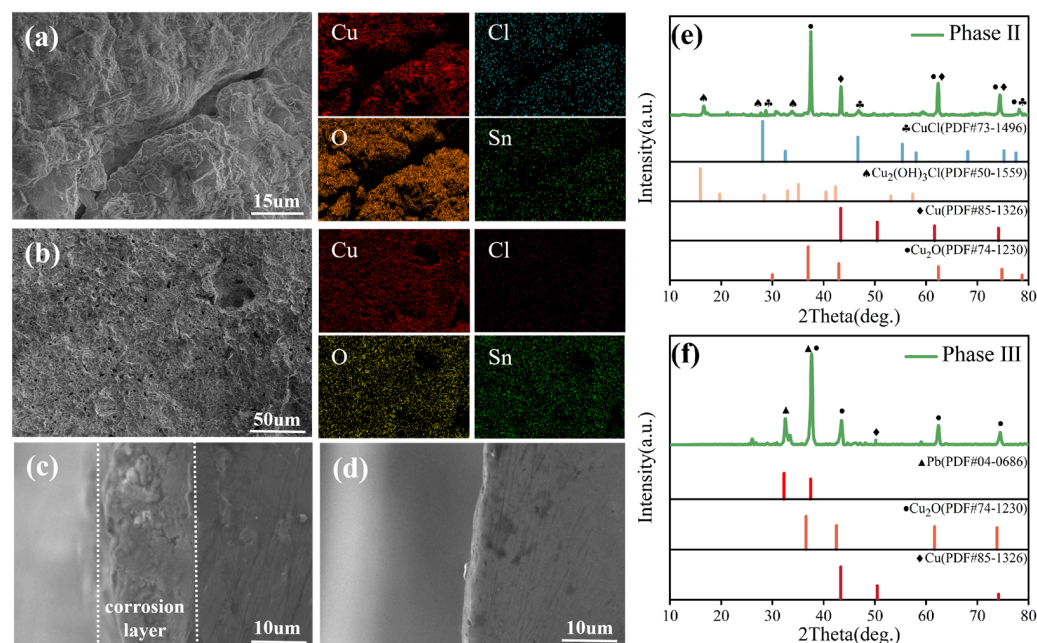


Figure 5. SEM and EDS images of Phase II and III samples (a,b); cross-sectional SEM images of Phase II and III samples (c,d); XRD patterns of Phase II and III samples (e,f).

XRD analysis (Figure 5e,f) further corroborated the above results. Before treatment, the diffraction pattern of the Phase II sample displayed characteristic reflections of corrosion products assigned to paratacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$ ($2\theta \approx 16.3^\circ$ and 32.2° ; PDF #50-1559) and nantokite CuCl ($2\theta \approx 27.9^\circ$ and 47.8° ; PDF #73-1496). After cleaning, the intensities of these reflections were significantly reduced or disappeared, and a reflection attributable to residual Cu_2O (PDF #74-1230) remained visible in the Phase III pattern. The residual Cu_2O is consistent with the hydrolysis of nantokite during cleaning (Equation (4)), in which cuprous chloride is converted to Cu_2O with release of chloride. The reduction in the corrosion-product reflections should be interpreted with caution, because the XRD signal may originate from both the surface layer and the underlying substrate, and XRD is of limited sensitivity for thin or poorly crystalline surface phases. In particular, no phosphate-containing crystalline phase was detected after cleaning, which is consistent with a thin or amorphous residual layer but does not prove its existence. Possible additional phases such as CuO and Sn-containing oxides were considered, but no reflections attributable to these phases could be unambiguously identified in the Phase III pattern. The combined SEM, EDS and XRD analyses indicate that the selected APP-boric acid-OP-10 cleaning system removes the loose, chlorine-containing outer corrosion products while preserving the compact inner layer.

3.4. Electrochemical Analysis

Figure 6a shows the open-circuit potential (OCP) of the three specimen phases as a function of immersion time. During the first 10 min of immersion, the OCP shifted negatively and

then gradually stabilized. The steady-state OCP of the cleaned (Phase III) specimens was more positive than that of the corroded (Phase II) specimens, indicating a reduced tendency toward active dissolution after cleaning. OCP is a mixed potential determined by the balance of anodic and cathodic reactions and does not by itself quantify the corrosion rate; the polarization and EIS results are therefore used as the primary electrochemical evidence.

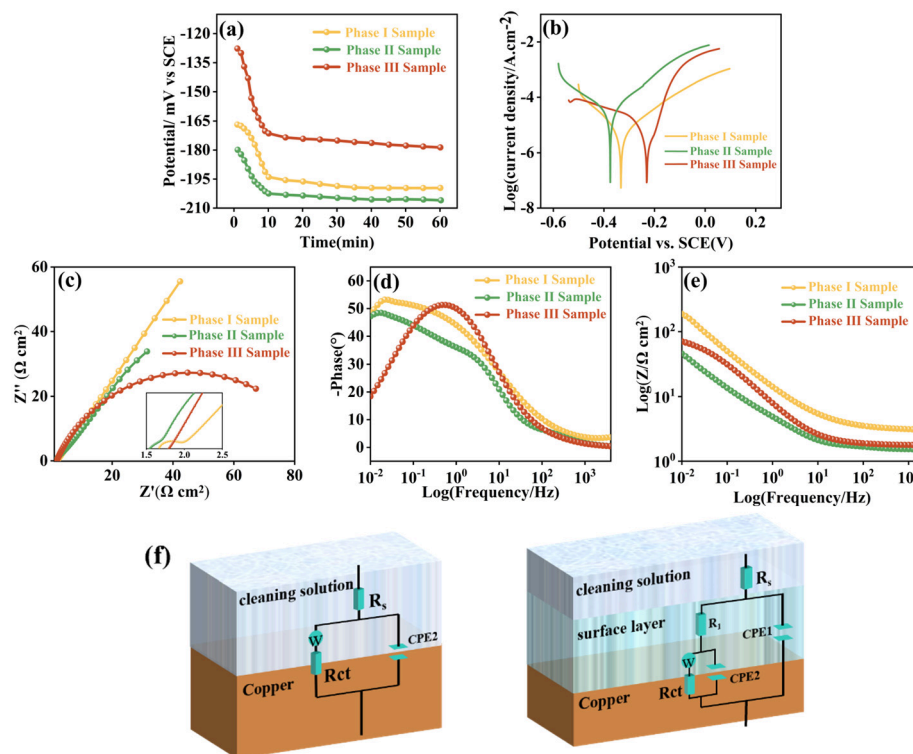


Figure 6. Electrochemical corrosion behaviour of bronze specimens in 3.5 wt% NaCl solution: (a) Open-circuit potential (OCP) vs. time curves; (b) Potentiodynamic polarization curves; (c) Nyquist plots; (d) Bode phase angle plots; (e) Bode modulus plots; (f) Equivalent electrical circuit used for EIS data fitting.

Figure 6b shows the potentiodynamic polarization curves of the three specimen phases, measured at a scan rate of 1 mV s^{-1} to approach steady-state conditions. The electrochemical parameters obtained by Tafel extrapolation are listed in Table 2. From Phase I to Phase II, E_{corr} shifted negatively from $-330 \pm 11 \text{ mV}$ to $-377 \pm 9 \text{ mV}$ and I_{corr} increased from $3.1 \pm 0.5 \mu\text{A cm}^{-2}$ to $8.8 \pm 1.2 \mu\text{A cm}^{-2}$, indicating that the artificial corrosion treatment accelerated the corrosion of the samples. After cleaning (Phase II to Phase III), E_{corr} shifted positively to $-225 \pm 5 \text{ mV}$ and I_{corr} decreased markedly to $1.5 \pm 0.5 \mu\text{A cm}^{-2}$. The reduction in I_{corr} indicates a decreased substrate dissolution rate in the short-term tests, suggesting that the cleaning treatment inhibited the corrosion reaction. This improvement may arise from the removal of the loose, chlorine-containing corrosion layer, and/or the presence of the residual compact Cu_2O layer, with a possible additional contribution from the adsorption of residual phosphate species on the exposed substrate, which may partially block active dissolution sites; these contributions are discussed in detail in the following EIS analysis. All remain plausible on the present evidence, and none has been demonstrated directly.

Figure 6c–e present the EIS results for the samples at the three treatment phases. The Nyquist plots (Figure 6c) show that all samples exhibited capacitive behaviour. The high-frequency contribution of the R_1 – CPE_1 pair (Phases II and III) is small and not resolved as a distinct arc, consistent with the low R_1 values; the dominant arc is therefore governed by the R_{ct} – CPE_2 pair. The Phase II sample had the smallest capacitive loop radius, followed

by the Phase I sample, while the Phase III sample had the largest. A larger capacitive loop radius in the Nyquist plot indicates greater resistance to the charge transfer process and a lower rate of interfacial electrochemical reactions. Therefore, the largest capacitive loop radius of the Phase III sample indicates that its surface possessed the strongest charge transfer blocking capability, which is consistent with the Tafel polarization results.

Table 2. Tafel Polarization Curve Data.

Phase	E_{corr} (mV vs. SCE)	I_{corr} ($\mu\text{A cm}^{-2}$)
I	-330 ± 11	3.1 ± 0.5
II	-377 ± 9	8.8 ± 1.2
III	-225 ± 5	1.5 ± 0.5

Values are the mean $\pm$ SD of three parallel specimens.

Equivalent circuit fitting of the EIS curves was performed using ZView software, with the equivalent circuit model shown in Figure 6f, and the fitted electrochemical parameters are listed in Table 3. In this model, R_s represents the solution resistance; R_1 is an empirical resistance element associated with ionic transport within residual surface layers; CPE (constant phase element) represents the capacitive behaviour, where CPE_1 can represent the response of a residual surface layer; R_{ct} is the interfacial charge transfer resistance, reflecting the corrosion susceptibility of the metal sample; and CPE_2 can be considered as the double-layer capacitance of the interfacial region. For Phase I (bare substrate without a corrosion-product layer), the simpler circuit without R_1 and CPE_1 was used, because no surface-film element is expected on the as-prepared metal; the comparison of R_{ct} values obtained with different circuit models is therefore semi-quantitative. The R_1 values for Phases II and III (0.07 and $0.23 \Omega \cdot \text{cm}^2$) are small in magnitude and are therefore retained as empirical elements. The interfacial charge transfer resistance R_{ct} follows the order Phase II < Phase I < Phase III (427 , 1264 and $3618 \Omega \cdot \text{cm}^2$, respectively), with the value for Phase III markedly higher than those of the other two phases. A larger R_{ct} value indicates more pronounced hindrance to the charge transfer process on the metal surface, thereby effectively reducing the corrosion reaction rate. Within the short-term measurement window of this work (1 h immersion), these results indicate that the cleaned surface exhibits improved corrosion behaviour; whether this reflects a genuine long-term improvement in corrosion resistance requires longer-term monitoring, which is beyond the scope of the present study. The substantial increase in R_{ct} and the decrease in I_{corr} suggest that the cleaning process removes the active, chlorine-rich corrosion products and leaves a more resistive surface. One possible contributing mechanism is that residual phosphate species adsorb onto the exposed copper substrate and form a thin layer that partially blocks active dissolution sites and retards charge transfer; alternatively, the residual compact Cu_2O layer may account for the increased R_{ct} . Surface-sensitive characterization would be required to distinguish these contributions.

Table 3. Equivalent Circuit Parameter Data.

Sample	R_s ($\Omega \cdot \text{cm}^2$)	R_1 ($\Omega \cdot \text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	CPE_1 ($\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2}$)	n_1	CPE_2 ($\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2}$)	n_2	χ^2 ($\times 10^{-4}$)
I	1.61 ± 0.09 (2.4%)	/	1264 ± 110 (4.4%)	/	/	0.017 ± 0.002 (5.8%)	0.78 ± 0.02 (1.1%)	3.2
II	1.54 ± 0.17 (3.9%)	0.07 ± 0.03 (14%)	427 ± 74 (7.1%)	0.006 ± 0.0008 (11%)	0.68 ± 0.05 (7%)	0.078 ± 0.011 (6.5%)	0.73 ± 0.04 (2.3%)	4.6
III	1.77 ± 0.06 (3.2%)	0.23 ± 0.07 (18%)	3618 ± 620 (5.6%)	0.005 ± 0.0007 (8%)	0.79 ± 0.03 (1.9%)	0.032 ± 0.004 (3.2%)	0.81 ± 0.02 (1.4%)	2.1

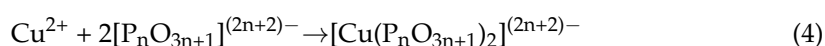
R_s , R_1 , R_{ct} , CPE and n values are the mean $\pm$ SD of three parallel specimens; numbers in parentheses are the relative fitting errors (%) of the individual parameters as output by ZView; χ^2 values are the goodness-of-fit of the representative fits shown.

The CPE parameters were not converted into effective capacitances or equivalent thicknesses in this work, because the different circuit models used for the three phases and the uncertainty in the CPE parameters preclude a reliable quantitative comparison. Qualitatively, the markedly higher capacitance associated with CPE₂ of the corroded Phase II sample and its decrease after cleaning are consistent with the removal of the loose, porous outer corrosion layer.

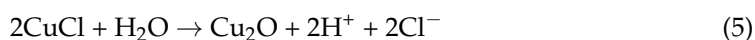
4. Proposed Cleaning Mechanism

In corrosive environments, various copper corrosion products form on the bronze substrate surface. Among them, nantokite (CuCl), which forms at the metal/corrosion-layer interface, can hydrolyse in the presence of moisture and oxygen to release chloride ions that re-attack the metal substrate, sustaining a continuous cyclic corrosion that severely threatens the structural integrity of the substrate [42–44]; basic copper chlorides such as paratacamite (Cu₂(OH)₃Cl) accumulate as characteristic products of this cycle. These corrosion products typically adhere to the metal surface as a porous layered structure; they not only obscure the inscriptions and decorative patterns on the copper coin surface but may also continuously participate in the corrosion reaction, thereby accelerating the degradation of the bronze substrate. Therefore, it is necessary to effectively remove these corrosion products during the cleaning process while avoiding the excessive corrosion of the metal substrate.

Ammonium polyphosphate (APP), as the core component of the composite cleaning solution, undergoes dissolution and partial hydrolysis in aqueous solution, generating phosphate species; these species include orthophosphate, pyrophosphate and oligomeric polyphosphate anions. The pyrophosphate and oligomeric polyphosphate anions can coordinate with Cu²⁺ released from the copper corrosion products and form water-soluble complexes [45], whereas orthophosphate tends to precipitate sparingly soluble Cu₃(PO₄)₂, which may contribute to the residual surface layer discussed in Section 4.2. Consistently, phosphate ions have been shown to inhibit the corrosion of copper and copper alloys in chloride-bearing waters through the formation of phosphate-containing surface species [46]. Specifically, the phosphate species can undergo complexation reactions with Cu²⁺ to generate water-soluble copper phosphate complexes:



The stoichiometry and charge balance of Equation (4) depend on the chain length of the polyphosphate anion. For the pyrophosphate anion ($n = 2$), the reaction is $\text{Cu}^{2+} + 2\text{P}_2\text{O}_7^{4-} \rightarrow [\text{Cu}(\text{P}_2\text{O}_7)_2]^{6-}$; for oligomeric polyphosphates ($2 \leq n < 20$), it follows the general scheme $\text{Cu}^{2+} + 2[\text{P}_n\text{O}_{3n+1}]^{(n+2)-} \rightarrow [\text{Cu}(\text{P}_n\text{O}_{3n+1})_2]^{(2n+2)-}$. Stability constants of Cu²⁺–pyrophosphate complexes have been determined under various conditions; for example, a cumulative formation constant of $\log \beta_2 = 8.87$ has been reported for $\text{Cu}^{2+} + 2\text{P}_2\text{O}_7^{4-} \rightleftharpoons [\text{Cu}(\text{P}_2\text{O}_7)_2]^{6-}$ in tetramethylammonium nitrate medium ($\mu = 1.0$) at 25 °C [47]. Owing to their negatively charged, hydrophilic nature, these complexes are readily dispersed in aqueous solution and transported away from the copper substrate surface during the elution process, contributing to the efficient removal of the corrosion layer.



It should be noted that the working solution is near-neutral: the measured pH of the fresh solution (4 wt% APP, 4 wt% boric acid, 0.5 vol% OP-10) was 6.88, and it decreased only slightly to 6.84 after the standard 30 min treatment, i.e., a drift of ≈ 0.04 pH units (Section 3.2.2; the pH measurements, including the calibration record, single-component values, and the titration

curve, are detailed in the Supplementary Materials, Tables S1 and S2 and Figure S4). Boric acid (pK_a 9.24) is largely undissociated at this pH and contributes little to the buffering; the pH is governed mainly by the phosphate buffer system of the APP ($pK_{a2} \approx 7.2$), as confirmed by the titration curve of the working solution (Figure S4), which exhibits a broad buffer plateau (pH 6.84 $\rightarrow$ 4.87 within 0–20 mL of 1 mol/L HNO_3) and an end-point at ≈ 26 mL. The small residual drift is attributed to the slow hydrolysis of the short-chain polyphosphate, which releases H^+ , and to the release of H^+ in the hydrolysis of nantokite (Equation (5)). Because the magnitude of the drift depends on the solution-volume-to-artefact-surface-area ratio, all cleaning tests in this work were performed at a fixed ratio of ~ 14.3 mL/cm² (100 mL per specimen, Section 2.2.2), and this ratio should be specified when the formulation is applied in practice (Section 4.2).

Regarding the marked increase in removal efficiency upon boric acid addition (66% $\rightarrow$ 93%; Section 3.2.2), the present data show that this effect cannot be attributed to the modest pH shift alone (≈ 0.6 pH units at 4 wt% boric acid). Although boric acid (pK_a 9.24) is largely undissociated at pH ≈ 6.9 and exerts little direct buffering, its addition progressively lowered the solution pH (7.48 $\rightarrow$ 6.06) and may thereby shift the speciation of the polyphosphate system: a modest pH decrease promotes the hydrolysis of short-chain polyphosphates towards shorter-chain species such as pyrophosphate, which form complexes with Cu^{2+} of higher stability, and the possible formation of B–O–P species may reduce the free orthophosphate available to precipitate sparingly soluble $Cu_3(PO_4)_2$, favouring the sustained dissolution of the corrosion products. These interpretations remain hypotheses; distinguishing them would require direct speciation measurements (e.g., ^{31}P NMR), which are listed as future work.

The nonionic surfactant OP-10 contains both hydrophilic and hydrophobic groups and exhibits typical amphiphilicity. This structural characteristic can significantly reduce the interfacial tension between the cleaning solution and the corrosion layer on the copper coin surface, allowing the solution to spread more easily on the hydrophobic corrosion layer and to penetrate inward along its microcracks and pores. Because OP-10 is a nonionic octylphenol ethoxylate (APEO), its possible residual adsorption on the artefact surface, the rinsing requirements, and its environmental and regulatory profile deserve consideration; these aspects are discussed in Section 4.1. After cleaning, the exposed active sites on the copper substrate surface may promote the interfacial adsorption of residual phosphate species from the solution. It is plausible that phosphate species coordinate with Cu atoms or trace amounts of Cu^+/Cu^{2+} on the substrate surface, leading to the formation of a phosphate-containing surface layer. A proposed mechanism is that the P–O groups on phosphate chains form coordination bonds with the vacant orbitals of surface Cu atoms, and multiple coordination sites act simultaneously to stabilize adsorbed phosphate species on the substrate. However, the continuity, thickness, and chemical structure of this surface layer remain to be directly characterized by surface-sensitive techniques such as XPS or FTIR, and the possibility that the improved corrosion behaviour arises primarily from the removal of active chloride-containing phases, or from the residual compact Cu_2O layer, rather than from a continuous conversion film, cannot be excluded (Figure 7).

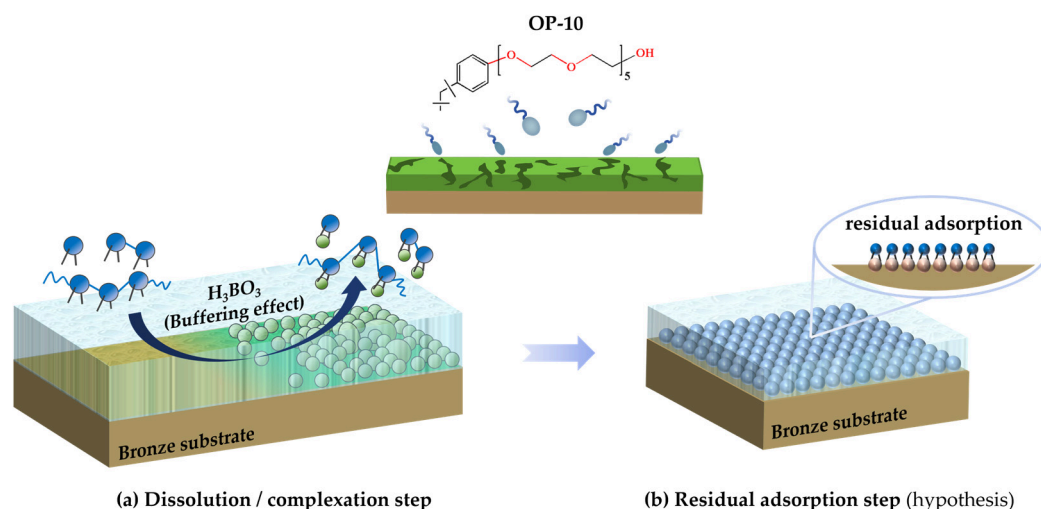


Figure 7. Schematic illustration of the proposed cleaning mechanism of the APP–boric acid–OP-10 composite system: (a) dissolution/complexation of the corrosion products and elution of the soluble complexes; (b) residual adsorption stage. The adsorption stage in (b) is a hypothesis that has not been directly characterized.

4.1. Safety, Environmental and Regulatory Considerations

OP-10 is an octylphenol ethoxylate (APEO). APEOs are subject to restriction within the European Union, and 4-tert-octylphenol is included in the Candidate List of Substances of Very High Concern (SVHC) owing to its endocrine-disrupting properties. Boric acid at 4 wt% is classified H360FD (may damage fertility; may damage the unborn child) and is likewise included in the SVHC Candidate List. For a formulation intended for heritage conservation applications, the following aspects must therefore be considered in any real application: (i) the rinsing efficacy after cleaning and the possible residual adsorption of OP-10 on the bronze surface; (ii) the long-term fate of residual phosphate and borate species within the artefact porosity, including the possible hydrolysis of condensed phosphates to orthophosphate with the attendant risk of biological colonization; (iii) the disposal of phosphate-rich effluents in accordance with local regulations; and (iv) occupational hygiene during manual handling and operation of heated baths. Where a conservation laboratory requires a more favorable regulatory profile, OP-10 could be replaced by alternative non-ionic surfactants such as alkyl polyglucosides, fatty alcohol ethoxylates or polysorbates; such substitutions were not tested in the present work.

4.2. Limitations and Applicability

Several limitations of the present study should be acknowledged. First, the experiments were performed exclusively on commercially available imitation coins; no genuine archaeological object was treated, and the corrosion stratigraphy produced by the accelerated protocol (chloride phases in the outer layer) differs from that of many archaeological bronzes, in which nantokite typically forms beneath the compact cuprite layer. Because the proposed treatment removes the outer layer and preserves the inner one, on real artefacts it may leave in place the chlorides responsible for bronze disease; its application to archaeological objects therefore requires case-by-case evaluation, and the conclusions drawn here pertain to simulated specimens. Second, the substrate-preservation assessment is based on gravimetric and microscopic evidence; quantitative determination of the Cu, Sn and Pb released into the cleaning solution was not performed. Third, the nature, continuity and thickness of any residual phosphate-containing layer remain uncharacterized. Fourth, the electrochemical evaluation reflects short-term behaviour and does not constitute an assess-

ment of long-term corrosion resistance. Finally, the regulatory profile of the components must be considered before any operational use.

5. Conclusions

This study developed a ternary composite cleaning system composed of 4 wt% APP, 4 wt% boric acid and 0.5 vol% OP-10 for the removal of corrosion products from simulated bronze surfaces. Under mild conditions, the system removed loose chlorine-containing corrosion products such as paratacamite, preserved the well-adherent compact inner layer, and controlled the colour change within an acceptable range. The proposed mechanism involves three coordinated steps: OP-10 reduces the interfacial tension to enhance the wetting and penetration of the solution into the porous corrosion layer; boric acid modulates the working solution to a near-neutral pH; and phosphate species generated by the dissolution and hydrolysis of APP form water-soluble complexes with Cu^{2+} , continuously withdrawing dissolved copper ions from the reaction interface and thereby shifting the dissolution equilibrium of the corrosion products forward. In short-term electrochemical tests, the cleaned surface exhibited improved corrosion behaviour, with an increased R_{ct} and a decreased I_{corr} relative to the corroded state. This improvement may arise from the removal of active chlorine-containing corrosion products and/or the presence of a residual compact Cu_2O layer, while the possible adsorption of residual phosphate species could also contribute; these contributions could not be fully distinguished on the basis of the present data. The proposed phosphate-related mechanism therefore remains a hypothesis pending direct surface characterization. This work provides a simple chemical route for the mild cleaning of corroded bronze surfaces on simulated specimens and demonstrates the potential of polyphosphate-based systems for enhancing the post-cleaning corrosion behaviour of copper alloys.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings16101196/s1>. Figure S1: Certificate of Analysis (CoA) of the ammonium polyphosphate (APP) supplied by Shanghai Macklin Biochemical Technology Co., Ltd. (Product No. AB75114-100g; CAS 68334-23-1; inspection date 1 April 2026); Figure S2: XRD pattern of the APP product (short-chain, crystalline form I); Figure S3: Characterization of the 4 wt% APP aqueous solution. (a,b) Dissolution test; (c) Centrifugation stability test; Figure S4: Potentiometric titration curve of the working solution; Table S1: pH meter calibration record (three-point calibration, 4.01/7.00/9.21; slope 97.8%); Table S2: Measured pH values of the freshly prepared solutions (20 °C); Table S3: Potentiometric titration records for the determination of chloride released into the working solution after the standard 30 min cleaning treatment.

Author Contributions: Conceptualization, N.X. and Z.P.; methodology, N.X.; validation, R.C.; formal analysis, R.C. and T.T.; investigation, R.C., T.T., K.X. and S.S.; resources, M.C. and H.X.; data curation, R.C. and J.W.; writing—original draft preparation, R.C.; writing—review and editing, N.X., X.C. (Xu Chen), J.Z. and X.C. (Xiaolian Chao); visualization, M.C.; supervision, J.Z. and X.C. (Xiaolian Chao); project administration, H.X. and X.C. (Xiaolian Chao); funding acquisition, J.Z. and X.C. (Xiaolian Chao). All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available in the article and the Supplementary Materials. The processed datasets (pH records and potentiometric titration records)

are provided in the Supplementary Materials; the raw datasets are available from the corresponding author upon reasonable request.

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References

- Chen, K.; Mei, J.; Rehren, T.; Liu, S.; Yang, W.; Martín-Torres, M.; Zhao, C.; Hirao, Y.; Chen, J.; Liu, Y. Hanzhong bronzes and highly radiogenic lead in Shang period China. *J. Archaeol. Sci.* **2019**, *101*, 131–139. [\[CrossRef\]](#)
- Li, H.; Chen, J.; Cui, J.; Wu, X.; Yang, Y.; Huang, F.; Xu, T. Production and circulation of bronzes among the regional states in the Western Zhou Dynasty. *J. Archaeol. Sci.* **2020**, *121*, 105191. [\[CrossRef\]](#)
- Megahed, M.M.; Elashery, N.H.; Saleh, S.M.; El-Shamy, A.M. Characterization, surface preparation, conservation, and corrosion protection of bronze arrow heads from Cairo military museum using nanocomposite coating. *SN Appl. Sci.* **2024**, *6*, 203. [\[CrossRef\]](#)
- Li, C.; Yang, B.; Shen, S.; He, B.; Luo, Y.; Jin, P. Preparation of micro-SiO₂-doped composite silane films and their corrosion inhibition performance on simulated bronze. *npj Herit. Sci.* **2025**, *13*, 572. [\[CrossRef\]](#)
- Sun, L.; Yang, G.; Liu, R.; Pollard, A.M.; Zhu, T.; Liu, C. Global circulation of silver between Ming–Qing China and the Americas: Combining historical texts and scientific analyses. *Archaeometry* **2020**, *63*, 627–640. [\[CrossRef\]](#)
- Chang, T.; Herting, G.; Goidanich, S.; Sánchez Amaya, J.M.; Arenas, M.A.; Le Bozec, N.; Jin, Y.; Leygraf, C.; Odnevall Wallinder, I. The role of Sn on the long-term atmospheric corrosion of binary Cu–Sn bronze alloys in architecture. *Corros. Sci.* **2019**, *149*, 54–67. [\[CrossRef\]](#)
- Zhang, L.; Yang, C.; Guo, Y. Corrosion and Protection of Chinese Bronze Relics: A Review. *Coatings* **2024**, *14*, 1196. [\[CrossRef\]](#)
- Zhang, L.; Zhu, Y.-G.; Guo, R.; Ning, Y.; Feng, J.; Chen, X.-L.; Zhu, J.-F. PVA Composite Hydrogel Film for Rust Removal of an Ancient Chinese Fragile Bronze Artifact. *Langmuir* **2025**, *41*, 5312–5322. [\[CrossRef\]](#)
- Dwivedi, D.; Mata, J.P. Archaeometallurgical investigation of ancient artefacts' degradation phenomenon. *npj Mater. Degrad.* **2019**, *3*, 15. [\[CrossRef\]](#)
- Li, H.; Zhao, Y.; Wang, X.; Guo, H.; Ren, C.; Liu, C.; Xiang, L. Research Progress on Characterization Techniques for the Corrosion Behavior of Bronze Artifacts. *Materials* **2026**, *19*, 162. [\[CrossRef\]](#)
- Liu, Y.; Shen, J.; Yin, Y.; Hu, B.; Song, L. Multidimensional exploration in bronze restorative conservation under the synergistic perspective of chemistry and art: A systematic review. *npj Herit. Sci.* **2025**, *13*, 646. [\[CrossRef\]](#)
- Zhu, G.; Xu, Z.; Jin, Y.; Chen, X.; Yang, L.; Xu, J.; Shan, D.; Chen, Y.; Guo, B. Mechanism and application of laser cleaning: A review. *Opt. Lasers Eng.* **2022**, *157*, 107130. [\[CrossRef\]](#)
- Shen, Y.; Zhang, G.; Zhou, X. Identification of an unusual pale green material on the surface of an ancient Chinese bronze vessel and application of laser cleaning to its removal. *npj Herit. Sci.* **2023**, *11*, 87. [\[CrossRef\]](#)
- Di Francia, E.; Lahoz, R.; Neff, D.; de Caro, T.; Angelini, E.; Grassini, S. Laser-cleaning effects induced on different types of bronze archaeological corrosion products: Chemical-physical surface characterisation. *Appl. Surf. Sci.* **2021**, *573*, 150884. [\[CrossRef\]](#)
- Sonaglia, E.; Schifano, E.; Sharbaf, M.; Uccelletti, D.; Felici, A.C.; Santarelli, M.L. Bacterial Nanocellulose Hydrogel for the Green Cleaning of Copper Stains from Marble. *Gels* **2024**, *10*, 150. [\[CrossRef\]](#)
- Hu, Y.; Wei, Y.; Li, L.; Zhang, J.; Chen, J. Same site, different corrosion phenomena caused by chloride: The effect of the archaeological context on bronzes from Sujialong Cemetery, China. *J. Cult. Herit.* **2021**, *52*, 23–30. [\[CrossRef\]](#)
- MacLeod, I.D. Conservation of corroded copper alloys: A comparison of new and traditional methods for removing chloride ions. *Stud. Conserv.* **1987**, *32*, 25–40. [\[CrossRef\]](#)
- Boccaccini, F.; Riccucci, C.; Messina, E.; Pascucci, M.; Bosi, F.; Chelazzi, D.; Guaragnone, T.; Baglioni, P.; Ingo, G.M.; Di Carlo, G. Reproducing bronze archaeological patinas through intentional burial: A comparison between short- and long-term interactions with soil. *Heliyon* **2023**, *9*, e19626. [\[CrossRef\]](#)
- Pagano, S.; Balassone, G.; Germinario, C.; Grifa, C.; Izzo, F.; Mercurio, M.; Munzi, P.; Pappalardo, L.; Spagnoli, E.; Verde, M.; et al. Archaeometric Characterisation and Assessment of Conservation State of Coins: The Case-Study of a Selection of Antoniniani from the Hoard of Cumae (Campania Region, Southern Italy). *Heritage* **2023**, *6*, 2038–2055. [\[CrossRef\]](#)
- Abate, F.; De Bernardin, M.; Stratigaki, M.; Franceschin, G.; Albertin, F.; Bettuzzi, M.; Brancaccio, R.; Bressan, A.; Morigi, M.P.; Daniele, S.; et al. X-ray computed microtomography: A non-invasive and time-efficient method for identifying and screening Roman copper-based coins. *J. Cult. Herit.* **2024**, *66*, 436–443. [\[CrossRef\]](#)

21. Oddy, W.A.; Hughes, M.J. The Stabilization of 'Active' Bronze and Iron Antiquities by the Use of Sodium Sesquicarbonate. *Stud. Conserv.* **1970**, *15*, 183–189. [[CrossRef](#)]
22. Sease, C. Benzotriazole: A Review for Conservators. *Stud. Conserv.* **1978**, *23*, 76–85. [[CrossRef](#)]
23. Selwyn, L.; Tse, S. The chemistry of sodium dithionite and its use in conservation. *Stud. Conserv.* **2008**, *53*, 61–73. [[CrossRef](#)]
24. Strifas, A.; Budinski, M.K.; Komarnicki, E.; McAtee, N.B.; Fox, M.; Mueller, E.; Zakar, F. The Efficacy of a Chelating Agent-Based Oxide Remover to Clean Corrosion Products from Ferrous Fracture Surfaces. *J. Fail. Anal. Prev.* **2019**, *19*, 1860–1865. [[CrossRef](#)]
25. Macchia, A.; Colasanti, I.A.; Rivaroli, L.; Favero, G.; de Caro, T.; Pantoja Munoz, L.; Campanella, L.; La Russa, M.F. Natural based products for cleaning copper and copper alloys artefacts. *Nat. Product. Res.* **2021**, *37*, 1177–1184. [[CrossRef](#)]
26. Joseph, E.; Cario, S.; Simon, A.; Wörle, M.; Mazzeo, R.; Junier, P.; Job, D. Protection of Metal Artifacts with the Formation of Metal-Oxalates Complexes by *Beauveria bassiana*. *Front. Microbiol.* **2011**, *2*, 270. [[CrossRef](#)]
27. Baglioni, M.; Poggi, G.; Chelazzi, D.; Baglioni, P. Advanced Materials in Cultural Heritage Conservation. *Molecules* **2021**, *26*, 3967. [[CrossRef](#)]
28. Domingues, J.A.L.; Bonelli, N.; Giorgi, R.; Fratini, E.; Gorel, F.; Baglioni, P. Innovative Hydrogels Based on Semi-Interpenetrating p(HEMA)/PVP Networks for the Cleaning of Water-Sensitive Cultural Heritage Artifacts. *Langmuir* **2013**, *29*, 2746–2755. [[CrossRef](#)]
29. Bosch-Roig, P.; Ranalli, G. The safety of biocleaning technologies for cultural heritage. *Front. Microbiol.* **2014**, *5*, 155. [[CrossRef](#)]
30. Pacheco, M.F.; Pereira, A.I.; Branco, L.C.; Parola, A.J. Varnish removal from paintings using ionic liquids. *J. Mater. Chem. A* **2013**, *1*, 7016–7018. [[CrossRef](#)]
31. McNeill, L.S.; Edwards, M. Phosphate inhibitor use at US utilities. *J. AWWA* **2002**, *94*, 57–63. [[CrossRef](#)]
32. Lytle, D.A.; White, C.P. The Effect of Phosphate on the Properties of Copper Drinking Water Pipes Experiencing Localized Corrosion. *J. Fail. Anal. Prev.* **2014**, *14*, 203–219. [[CrossRef](#)]
33. Di Turo, F.; De Vito, C.; Coletti, F.; Mazzei, F.; Antiochia, R.; Favero, G. A multi-analytical approach for the validation of a jellified electrolyte: Application to the study of ancient bronze patina. *Microchem. J.* **2017**, *134*, 154–163. [[CrossRef](#)]
34. Appelbaum, B. Criteria for Treatment: Reversibility. *J. Am. Inst. Conserv.* **1987**, *26*, 65–73. [[CrossRef](#)]
35. Sease, C. Codes of ethics for conservation. *Int. J. Cult. Prop.* **1998**, *7*, 98–115. [[CrossRef](#)]
36. Petiti, C.; Toniolo, L.; Berti, L.; Goidanich, S. Artistic and Laboratory Patinas on Copper and Bronze Surfaces. *Appl. Sci.* **2023**, *13*, 11873. [[CrossRef](#)]
37. Constantinides, I.; Adriaens, A.; Adams, F. Surface characterization of artificial corrosion layers on copper alloy reference materials. *Appl. Surf. Sci.* **2002**, *189*, 90–101. [[CrossRef](#)]
38. Di Carlo, G.; Giuliani, C.; Riccucci, C.; Pascucci, M.; Messina, E.; Fierro, G.; Lavorgna, M.; Ingo, G.M. Artificial patina formation onto copper-based alloys: Chloride and sulphate induced corrosion processes. *Appl. Surf. Sci.* **2017**, *421*, 120–127. [[CrossRef](#)]
39. Mokrzycki, W.S.; Tatol, M. Colour difference ΔE —A survey. *MG&V* **2011**, *20*, 383–411.
40. Papadopoulou, O.; Vassiliou, P. The Influence of Archaeometallurgical Copper Alloy Castings Microstructure towards Corrosion Evolution in Various Corrosive Media. *Corros. Mater. Degrad.* **2021**, *2*, 227–247. [[CrossRef](#)]
41. Criaco, C.; Delfino, D.; Spotorno, R.; Piccardo, P. The Role of Metallography in the Study of Archaeological Metal Votive Statuettes from the National Archaeological Museum of Campobasso. *Heritage* **2026**, *9*, 21. [[CrossRef](#)]
42. Jiang, L.; Xia, Q.; He, T.; Dong, W. Rational construction of a protective layer for corroded bronze based on composite corrosion inhibitors. *npj Herit. Sci.* **2025**, *13*, 187. [[CrossRef](#)]
43. Abdelbar, M.; El-Shamy, A.M. Understanding soil factors in corrosion and conservation of buried bronze statuettes: Insights for preservation strategies. *Sci. Rep.* **2024**, *14*, 19230. [[CrossRef](#)]
44. Saraiva, A.S.; Figueiredo, E.; Águas, H.; Silva, R.J.C. Characterisation of Archaeological High-tin Bronze Corrosion Structures. *Stud. Conserv.* **2020**, *67*, 222–236. [[CrossRef](#)]
45. Kura, G. Ion-Exchange Study of the Complex Formation of Some Condensed Phosphate Oligomers with Al^{3+} AND Cu^{2+} Ion. *Phosphorus Res. Bull.* **2007**, *21*, 88–94. [[CrossRef](#)]
46. Yohai, L.; Schreiner, W.H.; Vázquez, M.; Valcarce, M.B. Phosphate ions as inhibiting agents for copper corrosion in chlorinated tap water. *Mater. Chem. Phys.* **2013**, *139*, 817–824. [[CrossRef](#)]
47. Schupp, O.E., III; Sturrock, P.E.; Watters, J.I. A Study of the Stability and Basicity of the Copper(II) Pyrophosphate Complexes Using the Dropping Amalgam Electrode. *Inorg. Chem.* **1963**, *2*, 106–112. [[CrossRef](#)]

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