

EXPERIMENTAL STUDY OF GAP-FILLING OF ANCIENT COMPLETELY CORRODED COPPER BOWL VIA NANO-POLYMERS

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Abstract

Completely mineralized copper bowl was removed from the burial environment and was preserved without conservation treatment for long time. Corrosion process-induced has created broken and loose parts arising fragility of the object resulted from the burial condition (major factor), post-excavation, poor storage, transport procedures and mishandling. Corrosion products and soil encrustations were characterized by X-ray diffraction and scanning electron microscopy with energy dispersive spectroscopy SEM/EDS. Experimental studies on selected nano-polymers were performed on simulated objects after accelerated aging to modify gap-filling process. Microballoon was used as filler for bulking nano-paraloid B72, nano-primal and nano-veova. They were evaluated by SEM, IR and accelerated thermal aging. Results demonstrate that the use of microballoon in acryloid with fiberglass is the best gap-filling that was used in the reconstruction of the bowl. Veova is considered the best alternative polymer to paraloid B72 for filling gaps.

Keywords: Corrosion; Loose Parts; Conservation; Gap-filling; Polymers; Filler.

Introduction

This work presents a case study on gap-filling of highly deteriorated archaeological copper bowl. It was excavated from terrestrial sites rich in salts, soil deposits were adhered to copper surface. The common status in the lifetime of metal artifacts is their presence in the burial environment [1]. In the soil, corrosion mechanism of metals is usually occurring by electrochemical formation of active cells, which find an electrolyte solution (water with soil salts). The formation of these cells will be increased in well-ventilated sandy soil that is partially filled with water, otherwise fine clay soil with poor ventilation should be less harmful [2]. There is an outer layer consists of burial materials (soil minerals with organic materials) associated with corrosion products of copper artifacts. Cuprite is the first layer occurring on the surface which leads to the darkness [3]. After excavation, the bowl was preserved at the Egyptian museum storage, where uncontrolled conditions.

Metal artefacts are susceptible to accelerated corrosion reactions once they are excavated and exposed to new environmental conditions. High relative humidity (RH) levels in a museum

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environment combined with high pollutant concentrations increase the corrosion rate of metals [4, 5]. It appears that relative humidity in the ratio 40-50% is a risk environment to activate bronze disease [6, 7]. Also, low amounts of acetic acid with chloride ions at 42% RH reacts with copper and activate bronze disease [8].

The appearance of uniform blue-green copper (II) hydroxy chloride patina on the object caused by chloride ions, but bronze disease is suspected when localized outbreaks of mounds of the basic copper chlorides atacamite and paratacamite (α and δ $\text{Cu}_2(\text{OH})_3\text{Cl}$) occur in powder form [9]. They are considered to be one of the most de corrosion destructive products, due to low stability caused by the pressure resulting from the growth of hygroscopic crystals [10, 11]. They expand in volume on conversion to one of the copper trihydroxychlorides as paratacamite then turn to atacamite. This creates physical stress resulting in cracking or fragmentation, so it is difficult to retain surface details [1,12].

Loss parts on corroded copper artifacts caused by burial environment, during excavations, poor storage, mishandling or transport procedures [13]. This is a harsh cycle that accelerates the corrosion process and eventually leads to a complete metallic transformation [14].

Conservation of highly mineralized objects

The first step must be to determine through examination whether or not the metal is strong enough to allow cleaning. Edges are very corroded, fragile and thin; it is preferable to strengthen before filling the gaps. It will be necessary to remove any foreign materials in order to ensure that polymers will be fully adhered to the surface [15], except the historic materials used in the gap filling; it is considered an integral part with the object. Radical treatment of the completely corroded bowl is supporting and consolidation of the body and gap-filling of the loss parts which are considered reconstruction of corroded fragments is necessary to restore the object form to understand its original function and increase the object stability. Most of treatment techniques can not improve the state of the completely corroded objects. So, conservation treatment is particularly complex process due to a unique concomitance of different problems such as the extreme fragility, loss parts and distortion of the pieces. Strengthening technique by gap-filling may involve braising or raising and reshaping the mineralized objects, it should be done by a qualified metal smith familiar with historical [13]. To save the remain metal in highly mineralized object, relative humidity is found to be sufficient below 40%; cuprous chloride will not undergo chemical reaction, which already incorporates a margin of safety [6,7]. Unstable metal objects are stored together in a small room or in a cabinet where RH can be kept low with a dehumidifier [16]. In general, cuprous chloride remains stable in the absence of both oxygen and moisture [8].

Previous work for gap-filling via polymers

Gap-filling is still a manual procedure which needs experience from restorer. The materials used in filling the gaps and cracks can be considered as an adhesive mixed with filler materials [13]. Comparison between chemical and physical properties of gap filling polymers is challenging because previous work is limited. Early conservation practice of lacunae and gap-filling was performed by traditional materials as natural resins, waxes, plaster of Paris or 'Tecknovie paste', red Aswan clay with fiber textile, epoxy and silicon resins [13,17] which have been developed recently. Selected polymers for gap filling are based on the state of the object and the surrounding conditions. The main arguments against the use of any resins in gap-filling of metal objects are their transparency and their comparative hardness and reversibility [18].

Shearman preferred to use polyester paste mixed with colored material to fill the gaps [19]. Also, Lane H. (1974) used the translucent polyester resin with fiberglass to make thin layers suitable for the missing parts [20]. The aim of this paper is to monitor the influence of relative humidity and temperature on polymers used in gap filling after.

Experimental

The choice of the gap-filling material was based on the physical properties of the materials used in the field of conservation, as well as the minimal intervention in terms of the decorative details of the object. The fillings could be visible to the naked eye of any observer at close inspection. Diverse polymers (Acryloid B72, nano-Primal and nano-Veova) were used in the experimental study to select the best one for gap-filling and supporting the completely corroded artifacts. X-ray diffraction and SEM/EDS were used in characterization of corrosion products and soil encrustations. Polymers mixed with the filler material were evaluated via visual investigation, SEM, IR, and accelerated thermal aging to identify the homogeneity and integration of polymer and the filler.

Nano-polymers were prepared at polymers lab, National research center, Egypt. Organic groups of polymers were linked with inorganic filler (microballoon) to perform the gap-filling. Dehydration of the polymers was performed in two conditions (room temperature, above 100°C). Films were exposed between (50-150°C). At this condition, water as a solvent was completely evaporated.

The selected polymers for experimental testing were Paraloid B72, nano-Primal, and nano-Veova, which were mixed with microballoon as a filler material.

Preparation of nano Paraloid B-72

Paraloid B-72 is one of the most stable thermoplastic resins available to the conservator [21]. Co-polymer Emulsion lattices consists of Ethyl Methacrylate (EMA) and Methyl acrylate (MA) [22] by composition ratio 70:33 was prepared by semi-continuous technique with different solid content varies from 10 to 50 ± 1%. The polymerization was carried out according to the following procedure: in a 250 ml three necked flask, the desired amount of the monomers, according to the selected composition ratio (70:30 EMA/MA) was dissolved the same volume of acetone in period of one hour using mechanical stirring (500 rpm). A redox initiation system composed of potassium persulphate PPS (0.27gm) and sodium bisulphite (SBS) (0.416 gm) were dissolved in 40 ml distilled water and added drop wise to the reaction mixture during 30 minutes. The polymerization reaction was carried out for 3 hours at 70°C under stirring at 500 rpm. The reaction mixture was cooled to 50°C and subsequently neutralized with aqueous ammonium hydroxide to reach a pH value of about 9 [23].

Preparation of nano Primal AC-33

Co-polymer Emulsion lattices consists of Ethyl acrylate (EA) and Methyl Methacrylate (MMA) by composition ratio 66:34 was prepared by semi-continuous technique with different solid content varies from 10 to 50±1%. The polymerization was carried out according to the following procedure: in a 250ml three necked flask, 1 gm of sodium dodecyl sulphate (SDS) was dissolved in distilled water (30ml). The desired amount of the monomers, according to the selected composition ratio (66:34 EA/MMA) was added and well emulsified in period of one hour using mechanical stirring (500rpm). A redox initiation system composed of potassium persulphate (PPS) (0.27gm) and sodium bisulphite (SBS) (0.416 gm) were dissolved in 40 ml distilled water and added drop wise to the reaction mixture during 30 minutes. The polymerization reaction was carried out for 3 hours at 70oC under stirring at 500 rpm. The reaction mixture was cooled to 50°C and subsequently neutralized with aqueous ammonium hydroxide to reach a pH value of about 9 [24].

Preparation of nano Vinyl Acetate - Veova copolymer

Polymerization of VAc/VeoVa10 lattices can be carried out in 250 ml equipped with an anchor or turbine stirrer, a cooling mantle, a nitrogen flux and reflux condenser. The monomer mixture and initiator solution are fed into the reactor with a pump. Water and the anionic emulsifiers are placed in the glass reactor and heated until 85°C. Then, water containing the initiator persulphate is added in the reactor. The reactor is heated to 85°C and 2.5% of pre-emulsion is added. On the other hand, a small amount of butyl acrylate (BuA) was used because

it has been observed that polymerization of vinyl esters starts much more readily in the presence of a small amount of (BuA). After 10 minutes, the rest of the pre-emulsion is then added during 3 hours (slowly at the beginning). After pre-emulsion addition the reactor is kept at 85°C for 2 hours and aqueous solution of sodium metabisulfite and Azobis were separately fed to the reactor during 30 minutes period to reduce the residual monomer. Then the latex is cooled down to room temperature and filtrated. A typical recipe for the preparation of 48% solids product is given in table 1 [25].

Table 1. The recipe for preparation of VAc/ VeoVa10 copolymer latex.

Ingredient	Amount (g)
Vinyl acetate	30-50
VeoVa10	0-20
Butyl acrylate	0.3
Sodium lauryl sulfate	2.0
potasium persulfate	0.5
Sodium metabisulfite	1.0
2-Azobis (2-methyl propionitrile)	0.25

Microballoon (Filler materials) is hollow, unicellular soda lime borosilicate glass microsphere. It may have a wide range of application in conjunction with materials commonly used by conservators, as fiberglass will not react with most resins. The possible degradation of the phenolic resin is not a problem as the balloons are totally encapsulated in the resin, and the fill itself is isolated from the substrate [18, 26].

Simulation Experiments

The experimental set up consisted in forged dishes which composed of (copper 99%-zinc 1%). Dimension of dishes is 16cm diameter and 0.1cm thickness. They were prepared by immersion in 40% acetic acid for 2 weeks which cause highly mineralized.

Case study

The dimension of the bowl is 28.5cm of the height, 9.5cm of the base diameter, 23.3cm of the rim diameter and 2-3mm in thickness increasing from the ream to the base (Fig. 1). The construction metal-alloy was investigated by scanning electron microscope. The sample was examined carefully in the unetched condition.

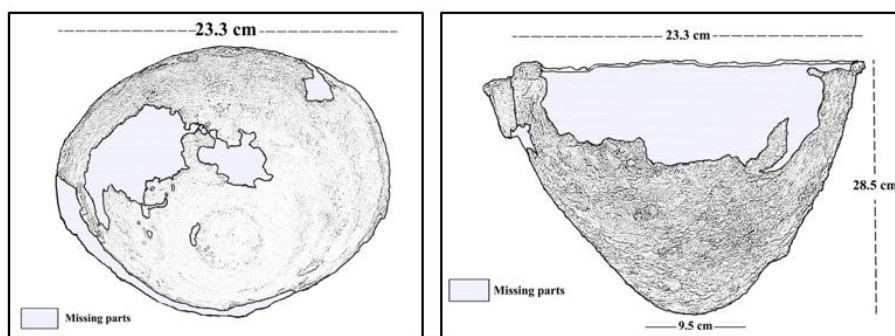


Fig. 1. Sketch for loss parts and the dimension of the ancient bowl.

Documentation of the bowl has been undertaken using photographic recording before, during and after conservation treatment (Fig. 2). Cross section of corrosion layer from the bowl is shown in (Fig. 3). Exterior layer is made up of green corrosion crusts mixed with soil deposits, but interior layer is mostly made up of cuprite.

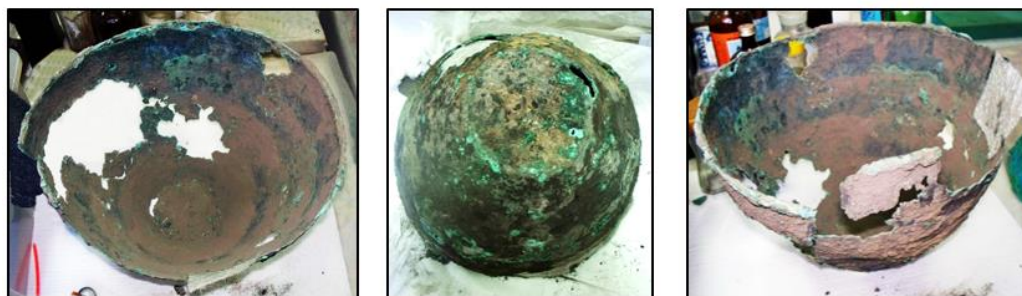


Fig. 2. Original condition of severe damage of corroded bowl before gap-filling treatment.

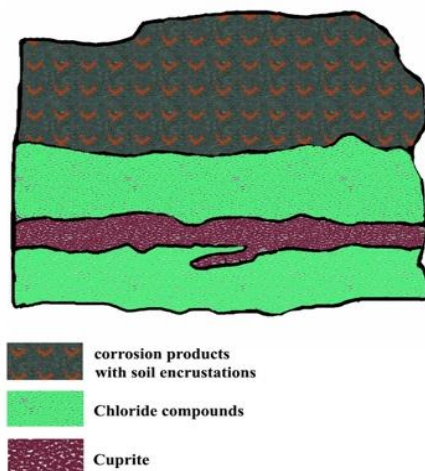


Fig. 3. Stratigraphic of corrosion products with soil encrustations.

Results and discussion

Simulation experiments

Direct dehydration of polymers mixed with microballoon above 100°C caused swollen of selected polymers which were observed by SEM (Fig.4), IR (Figs. 5-7) and mechanical properties (Table 2). Nano-Viova and nano-primal cannot detected by SEM/EDS resulted from water content, but paraloid B72 with microballoon was analyzed.

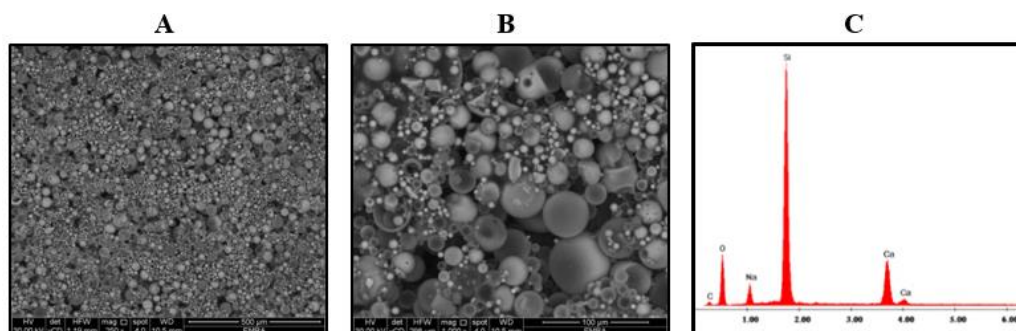


Fig. 4. SEM/EDS result of paraloid mixed with Microballoon: **A and B**: SEM image showing circular grains of microballoon in paraloid ground and the surface morphology; **C**: shows EDS analysis for the complete structure of microballoon.

Table 2. Considerations for selected polymers used in gap filling.

Polymers Evaluation methods	Paraloid		Primal		Vevoa	
	+ microballoon	+ microballoon + Fiberglass	+ microballoon	+ microballoon + Fiberglass	+ microballoon	+ microballoon + Fiberglass
Finishing appearance	++++	+++++	+	++	++	+++
Strength of the adhesion	+++++	+++++	+++	+++	+++++	+++++
Reversibility	+++++	+++++	+++++	+++++	+++++	+++++
Thermal stability	+++++	+++++	++	++	+++++	+++++
Inelasticity (Hardness)	+++++	+++++	++	+++	++	+++
Shrinkage	+	+	+++++	+++++	+++++	+++++

EDS analysis results of paraloid mixed with microballoon shows SiO₂ 64.66%, CO 17.80%, CaO 10.06% and Na₂O 7.47% caused by the elemental composition of microballoon which made of glass or phenolic material.

IR results demonstrate that solvents (water/acetone) used in the tested polymers affected on chemical structure. There was observed changes after thermal aging at 100°C for one hour for primal and nano-vevoa with microballoon, but both IR-spectrum (before and after aging) gives the similar peak shape (function groups).

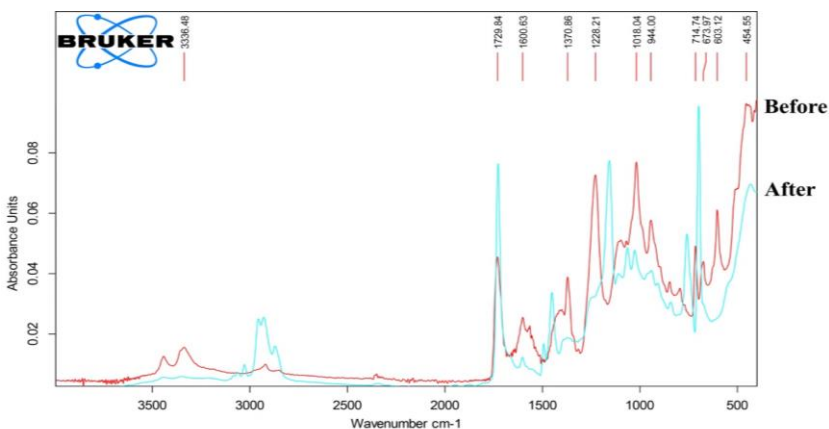


Fig. 5. IR spectra of primal mixed with microballoon before and after thermal aging.

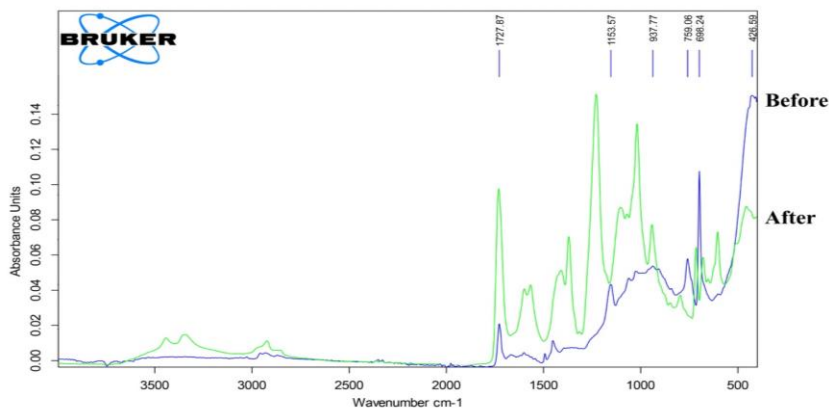


Fig. 6. IR spectra of vevoa mixed with microballoon before and after thermal aging.

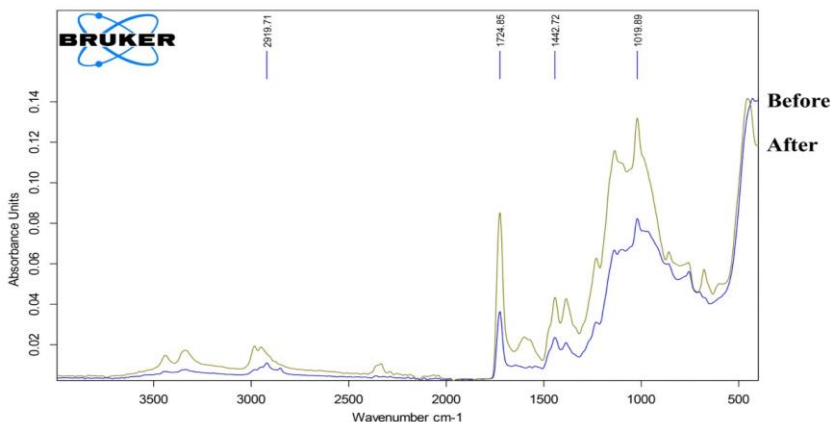


Fig. 7. IR spectra of paroloid mixed with microballoon before and after thermal aging.

The strength of the adhesion between polymer and the body of the dishes was increased when paroloid B-72 (90%), Veova (80%) and primal (60%) exposing to thermal aging.

Fiber-glass did not alter in physical properties after accelerated aging by temperature. The result of demonstrates that gap filling is likely to perform by using a paste composed of microballoons as a filler with Paraloid B72 supported with fiberglass.

Case study

Two samples, one from the interior and exterior layers were analyzed by powder x-ray diffraction. The detected corrosion products by XRD analysis were Cuprite (Cu_2O) with reference code 00-001-1142, Atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) with reference code 00-002-0146, Clinoatacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) with reference code 01-074-9146, Malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) with reference code 00-001-0959, Ammonium Copper Sulfide ($\text{NH}_4\text{Cu}_6.84\text{S}_4$) with reference code 01-089-5497 and Silicon dioxide (SiO_2) with reference code 01-073-3437 was detected as soil deposits (Fig. 8-9).

SEM/EDS analyses were performed by providing information on the corrosion patterns (Fig. 10-11). Imaging of the surface by SEM shows two zone, white and black. EDS analysis of the white zone include Cu 98.64% and Cl 1.36%. The black zone includes Cu 98.89%, Cl 0.72% and Ca 0.39%. Cl element could be attributed to basic copper chloride (Atacamite $\text{Cu}_2(\text{OH})_3\text{Cl}$) which was observed in XRD analysis. Ca element traces may originate from soil encrustations where the bowl was buried.

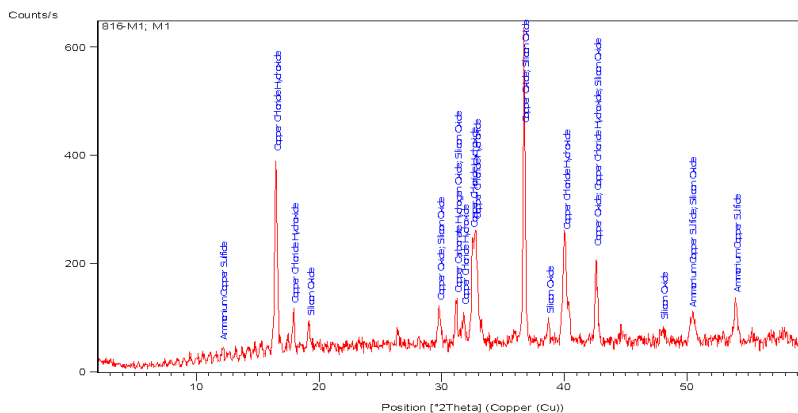


Fig. 8. XRD pattern of the corrosion products and adhering soil encrustations from the exterior layer.

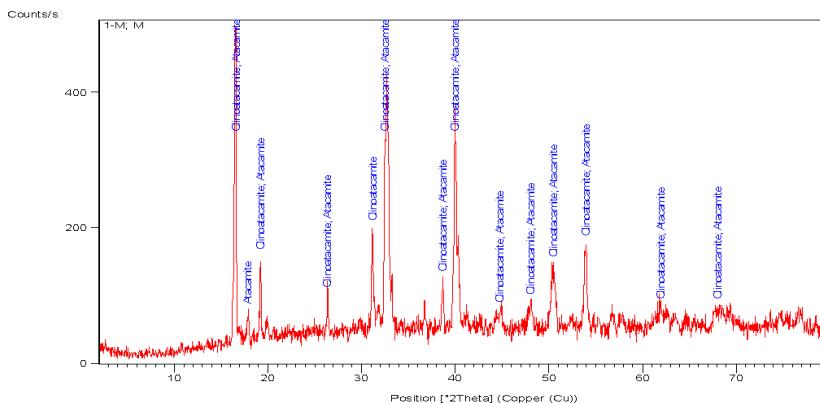


Fig. 9. XRD pattern of the corrosion products from the interior layer of the bowl.

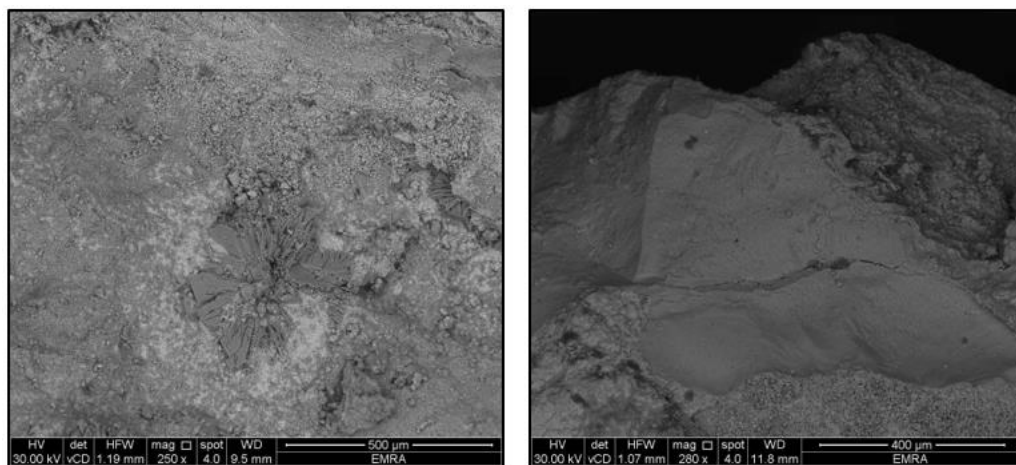


Fig. 10. SEM image showing the morphology of corrosion layers.

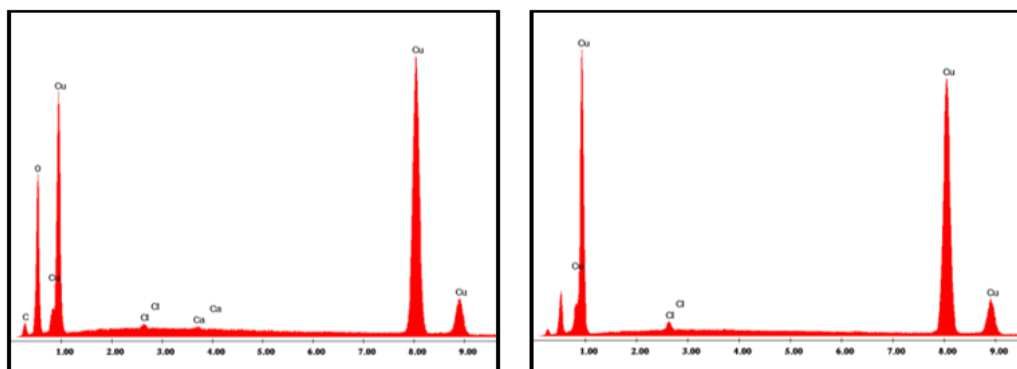


Fig. 11. EDS analysis results of the black (left) and white area (right) of the sample.

No previous repairs and restorations have done for the object. Examinations have shown that the metal is totally mineralized and cannot be able to withstand the simplest cleaning actions. Therefore, the bowl surface has been cleaned by using hand tools such as soft brushes

and scalpels to remove soil encrustations and corrosion products which formed both inside and outside the bowl (Fig. 12a). The process of gap filling with polymers may be appropriate to halt the corrosion activation.



Fig. 12. The restoration of the bowl: A - Soft brushes and scalpels have been used to remove soil encrustations and corrosion products; B - building up of fiberglass sheets; C - Gaps have been filled by the prepared paste; d - Bowl after finishing the treatment processes.

The reconstruction of the bowl was performed according to the original form. Prior starting the gap-filling process, the building up fiberglass was the most difficult stage which used a support from interior to strengthen the edges; due to the large extent of the missing parts.

The main concern was the extreme small thickness of the bowl, in combination with the large extent of the missing parts at the base and rim (Fig. 12b).

Filling the gaps, chips and cracks was performed by a paste (a mixture of 40% acryloid B72 with microballoon), runs around the outside. Foam sheets were also used inside the bowl to keep the thickness and durability of the filled gaps (Fig. 12c).

Conservation and restoration processes and finishes include the best form of packing was decided. The bowl surface was coated with 3% paraloid B72 (criss-cross manner) to guarantee the complete protection. Finally, these parts were coloured by 1% paraloid B72 with brown oxide.

SEM examination of bowl fragments shows three layers of corrosion were cracked and separated. With respect of the thin thickness surfaces, it may be distorting if the amount of used paste in gap-filling is increased, which will be led to damage the metal artifact.

The object was returned to the museum storage and was kept in the controlled environment after refitting the cabinet (Fig. 12d).

Conclusion

The copper bowl was suffering from a severe deterioration aspect, resulted in its total loss, which necessitated the need for reconstruction for rehabilitation this object. Experimental data demonstrate that paraloid B-72 mixed with microballoon was the best material, because it is reversible, transparent, and non-destructive. This paste was used for gap filling with fiberglass plates due to the large extent of the missing parts. Particulate microballoon is spherical which decrease the total content of polymer, at the time it improved the physical property of the polymer. Veova is considered the best alternative polymer to paraloid B72 for filling gaps.

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Received: May 14, 2019

Accepted: February 02, 2020