A SYSTEMATIC APPROACH TO BRONZE CORROSION PRODUCTS AND THE METHODS OF TREATMENT, APPLIED ON THREE BRONZE ANKLETS FROM DHAMAR MUSEUM, YEMEN.

by Mohamed M. Megahed

Three bronze anklets, found during the archaeological excavation of Yemeni mission 2002 A.D., in Gabal al- lawd, Jawf area, Yemen and, dated back to Minaean period in Yemen (sixth century B.C. - 24 B.C.),are now in Dhamar regional museum. They suffered deterioration: two of these anklets had a thick corrosion products of pale- green/brown, the third had a rust-colored Black and Brown with the presence of small parts and scattered pale green.

Numerous studies on ancient and historical bronzes have tried to establish the chemical characteristics and structure of natural patinas grown on artifacts exposed for long periods of time to soil, atmosphere, water or sea water. The long-term corrosion of bronzes is accompanied by structural transformations leading to a steady state. Different surface patterns have then been observed, depending on the corrosive environment (chemical composition, PH, resistivity, etc.) but also on other non-negligible parameters such as historical periods, metallurgical techniques or even kind and size of the artifacts [1].

Analytical investigations revealed that the main corroding agent is represented by chlorine containing species that induce the formation of dangerous copper chlorides and oxychlorides at the interface between the metal surface and the outer most corrosion products layers via a continuously occurring reaction. For many archaeological objects the reactive cuprous chloride (Cu Cl) species is considered as the principal agent of the so-called bronze disease, i.e. the process of interaction of chloride containing species within the bronze (patina) with moisture and air, accompanied by corrosion of the copper alloy itself. The cuprous chloride cyclically reacts with Oxygen and atmospheric water (humidity), thus giving rise to the formation of Atacamite2Cu2(OH)3Cl and its polymorphs. These oxy-chloride compounds react with copper to form cuprous chloride and water, and in this way Cu, Cl, O2 and H2O are converted in cuprite (Cu2O) and Atacamite (2Cu2(OH)3Cl) in a cyclical and continuous process. The final products of the reaction are light green, powdery, voluminous basic chlorides of copper , which disrupt the surface and may disfigure the artifacts .The nature and composition of the soil at the excavation site is of great importance for the degradation of the archaeological artifacts, but in the case of metal bronze objects, humidity and chlorides are the key factors [2].

Organ in the 1963 [3] proposed many equations for these reactions, but it is now generally recognized that these equations are too simplistic. They suggested that the principal mechanism is the production of cuprous oxide (Cuprite) by hydrolysis of cuprous chloride:

$$2CuCl + H_2O = 2HCl + Cu_2O$$

The hydrochloric acid generated by this reaction will then produce more cuprous chloride:

$$2HCl + 2Cu = 2CuCl + H_2$$

But Macleod 1987 [4] had pointed out that, the ΔG of reaction for equation is +16.3 kcal. mole−1, showing that the reaction will not proceed spontaneously because of the positive value of ΔG. In standard conditions, the positive sign of the ΔG of reaction for the hydrolysis of Nantokite means that the reaction cannot proceed as such without an additional thermodynamic driving force. In addition, Nantokite has a solubility of about 0.006 g per 100 ml of water at room temperature and, this low solubility limits the extent to which hydrolysis reactions may occur. It is possible to provide a thermodynamic thrust to the right hand side of Organ's equation, if the positive ΔG can be overridden by other factors. One of the factors that must be considered is the presence of alloying elements: tin in bronze or zinc in brass. There are, of course, electrochemical and kinetic factors to be considered here. Not only there are subtle electrochemical factors to be considered concerning the difference in potential between tin-rich phases and the copper-rich alpha phase in bronzes, but there are a variety of burial conditions to be considered [5]. The formation of these patinas in burial is ascribed to oxygen and carbon dioxide carried by ground waters. The salts present in soil solutions can influence the formation of the patina and the nature of the corrosion, but on the whole are of minor importance. The dissolution of copper and other divalent ions is solely due to the free carbon dioxide in the water and the progress of this dissolution is dependent on the concentration of carbon dioxide in solution. If this concentration is high, as for example in humus or porous sandy soils, then the patina is formed rapidly and the continuing dissolution of copper results in an end product of pure tin oxide, whereas in other soils, such as clay, bronzes of the same age may be covered only by a thin patina.

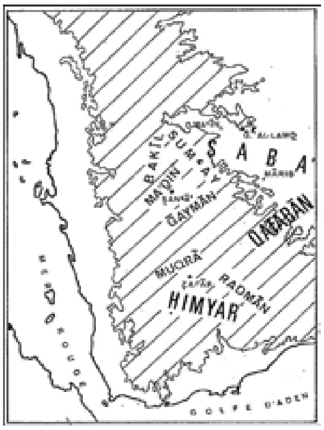

Fig. 1 - shows the location of Gabal-al lawd , Al-Gowf area ,Yemen. (After: Robin .C, Breton .J.F,1982, [7]).

In humus-rich sandy soils with low lime content, there is no inhibiting effect on the decomposition of the patina to create a tin oxide surface, while in lime containing soils, where the soil solutions may contain calcium bicarbonate, this decomposition is inhibited [6].

The purpose of the present paper is to start filling the lacks diagnosed above. First, by proposing a suitable methodology for the surface study of archaeological metals, then by focusing on binary Cu-Sn alloys, to get a deeper insight into the physical and chemical characteristics of bronze patinas. This was achieved through a systematic study for three bronze anklets dating back to the Minaean period (sixth century BC to 24 B.C.) and found during archaeological excavation in 2002 A.D. in Gabal-al-lawd, Al-Gowf area (fig. 1).

MATERIALS AND METHODS: DESCRIPTION AND CONDITION

The dimensions of the three anklets are similar in size and scale, the diameter of each anklet is about 8.5 cm.They suffered from the deterioration. The two others klets had a heavy crust of pale green corrosion products incorporating soil particles, disfiguring them and left them ugly (fig. 2).

Fig. 2 - shows the first side of the anklets before treatment.

EXAMINATION AND ANALYSIS

The three anklets were examined by metallographic and scanning electron Microscope. Corrosion products were analyzed by X-ray diffraction method (XRD) and the metallic portion by XRF.

METALLOGRAPHIC EXAMINATION (ME)

Examination of the three anklets shows the elongation of the metallic grains in the direction of hammering. this is in addition to the appearance of deteriorated spots dispersed on the metal surface as it is shown in (figs. 3,4,5).

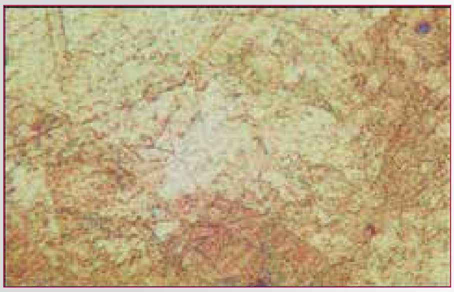

Fig. 3 - ME for a sample from the anklet A shows the Uniform corrosion (50X).

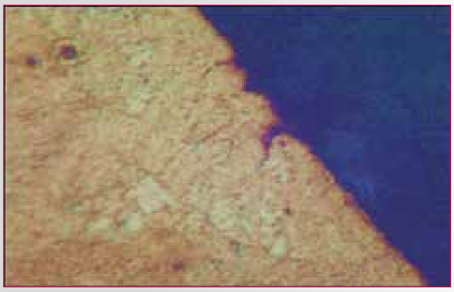

Fig. 4 - ME for a sample from the anklet B shows the Grieve corrosion (150X).

Fig. 5 - ME for a sample from the anklet C, suffers from pitting corrosion (50x).

SCANNING ELECTRON MICROSCOPIC EXAMINATION (SEM)

SEM examination of the anklets showed their deteriorated spots, which dispersed on the metal as it is shown in (figs. 6,7,8). This confirmed the results obtained by metallographic examination .

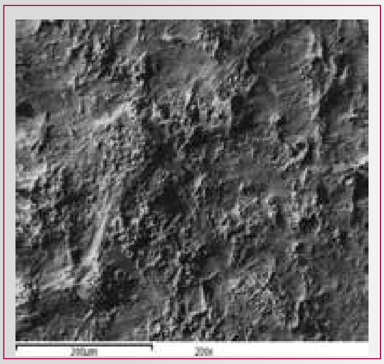

Fig. 6 - shows SEM examination for a sample from the anklet A, suffers from pitting corrosion and distorted surface (200X).

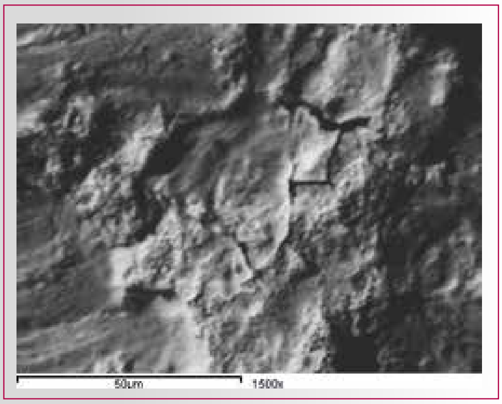

Fig. 7 - shows SEM examination for a sample from the anklet B, suffers from micro cracks & Grieve corrosion (1500X).

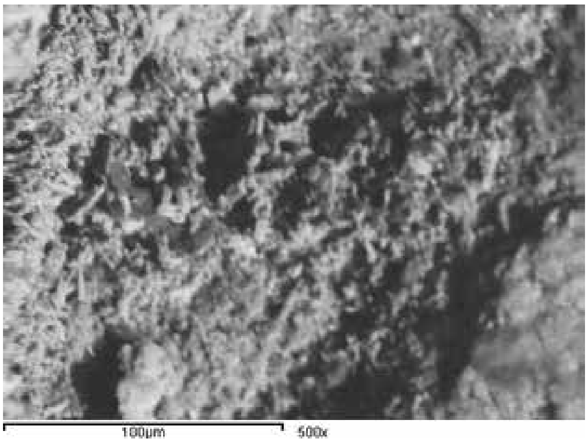

Fig. 8 - Shows SEM examination for a sample from the anklet C, suffers from pitting corrosion and distorted surface (500X).

X-RAY DIFFRACTION ANALYSIS (XRD)

Three small samples were taken from the corrosion products mixed with the soil residues covering the anklets and analyzed by using a Philips X-ray Diffractometer with Cu Kα radiation. The first sample was taken from the reddish brown layer that covered the anklet no. A, the second sample was taken from the pale greenish crust that covering the anklet no. B and the third sample was extracted by the pale greenish crust that covered the surface of the anklet C. The obtained diffraction-scans are reported in (figures. no.9,10,11) and the identified compounds in table 1.

X-ray diffraction patterns of the corrosion products of the anklets indicate that they consist essentially of Atacamite Cu_2 (OH)3Cl, Paratacamite Cu2(OH)3Cl and cuprite Cu2O.

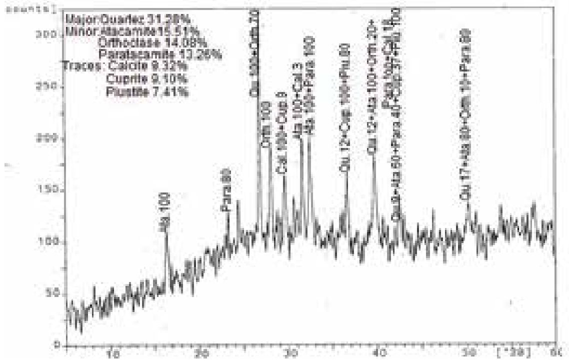

Fig. 9 - Shows XRD scan for the corrosion products of the anklet A.

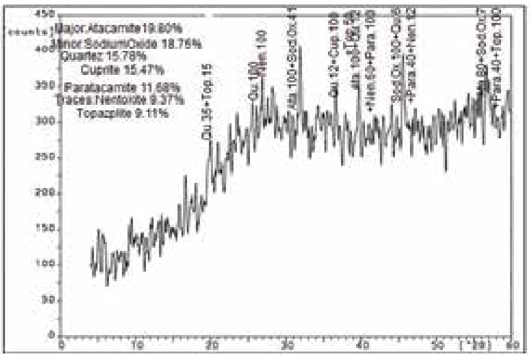

Fig. 10 - Shows XRD scan for the corrosion products of the anklet B.

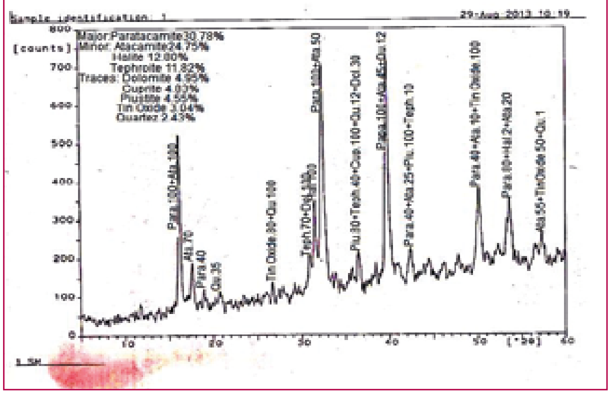

Fig. 11 - Shows XRD scan for the corrosion products of the anklet C.

Samples	Compounds		
	Major	Minor	Traces
-The anklet no. A	Quartez SiO2	Atacamite Cu2(OH)3Cl Orthoclase K Al Si3O8 ParatacamiteCu2(OH)3Cl	Calcite CaCo3 Cuprite Cu2O Piustite Fe O
-The anklet no . B	Atacamite Cu2(OH)3Cl	Sodium Oxide Na2O Quartez SiO2 Cuprite Cu2O ParatacamiteCu2(OH)3Cl	Nentokite Cu Cl Topazplite 3CaO.Fe2O3.3SiO2
-The anklet no. C	Paratacamite Cu2(OH)3Cl	Atacamite Cu2(OH)3Cl Halite Na Cl Tephroite Mn2SiO4	DolomiteCaMg(Co3)2 Cuprite Cu2O Piustite Fe O Casiterite Sn2O Quartez SiO2

Tab. 1 - Shows XRD analysis results of corrosion products of the anklets.

X-RAY FLUORESCENCE ANALYSIS (XRF)

X-Ray Fluorescence is a non-destructive, powerful and easy-to-use technique for the elemental analysis of a wide variety of materials. Three small samples from the anklets were analyzed exploiting this technique to determine their composition, by using a NITON/XL8138 (USA), driven with software version 4.2E. The results suggest a bronze alloy, with a high a mounts of Tin and traces from Lead, Iron and Zinc, as reported table 2.

Elements Samples	Cu%	S n%	P b%	Fe%	Zn %	Total %
-The anklet no. A	84.15	14.78	0.34	0 .61	0 .12	100
-The anklet no . B	83.08	15.96	0. 11	0.75	-	100
-The anklet no .C	81.62	16.83	0.07	1.13	0.35	100

Tab. 2 - Shows XRF analysis results of the anklets.

TREATMENT AND CONSERVATION

The use of chemical treatments for the anklets is more acceptable than the mechanical cleaning, as these anklets had a thick and crust layers, because the long period of buried in the soil and the strong interaction between the surrounding environment and the objects. It will be difficult to remove the concretion layers and the hard crusts by mechanical tools without damaging the surface by the pressure exerted during mechanical cleaning. In addition a preliminary examination proved that the anklets didn't have any figures or inscriptions on their surface. So the chemical treatment was chosen assisted by skilled mechanical cleaning to remove the loose corrosion products. A serial of tests were carried out to determine which chemical compounds would be effective without damage the objects the least by varying the concentration and time of contact, it was found the following chemical compounds are the least damaging and fastest acting solutions.

The treatment procedures included the following steps:

- Soaking the anklets in 10% solution of sodium hexametaphosphate to convert the insoluble calcium carbonate in the encrustation to soluble salt which can be subsequently washed away. This was done with regular checks and removing loosened particles with silk brush. This procedure was followed by repeatedly baths of deionized water with heating from time to time in order to loosen the concretion and hard layers of the corrosion products. This step resulted in dissolving and removing soil granules and the soluble corrosion products, and left the anklets have a hard crust of very adherent corrosion compounds.

- The three anklets were soaked in alkaline Rochelle solution that was changed many times assisted by gentle mechanical cleaning with silk brush from time to time to dissolving the corrosion layers of copper [II] compounds .this step succeeded in removing green copper corrosion products and left a red brown layer covering the anklets surfaces.

- To dissolve and remove the oxide layer [Cuprite], 3% solution of sulphuric acid was used assisted by a brush to remove the loosed layer, this was done with regular checks and removing loosened layer, these procedures succeeded in removing all the corrosion products.

- After that the anklets were soaked in water and washed by a tooth brush to dislodge residue from crevices.

- Repeated washing in hot deionized water altering heating and cooling to ensure flushing capillaries to remove any chemical residues.

- Drying in repeated bathes of ether followed by drying in hot sawdust and mopped dry with soft, clean cloth.

- Finally the anklets were isolated with paraloid B-72 dissolved 3% toluene and they were handed to Dhamar museum (see figures 12,13,14).

RESULTS AND DISCUSSION

- It is worth noting that the selected Cu-based archaeological objects have been produced by using the main manufacturing techniques employed in ancient time to produce bronze artifacts. The study declared that the ancient Yemeni manufacturer used both of casting and hammering technique to manufacture the three anklets.

- XRD analysis of the corrosion products have shown the presence of Copper and Tin species such as cassiterite [$SnO2$], cuprite [$Cu2O$], tenorite [Cu O], nantokite [Cu Cl], atacamite [$Cu2(OH)3Cl$] and paratacamite [$Cu2(OH2)Cl$]. The latter compounds are basic copper chloride and are very dangerous as corrosion products [8,9].The sandy soil where the three anklets were excavated played an important role in their severe corrosion. This soil is a porous one changed from sub saturation to saturation with water, had different salt ions, specially, the dangerous chlorine ion [10,11]. This circulation of saline water in the soil had a serious effect on the objects, which led to the formation of the bronze disease chloride components [12,13].

- The existing of bronze disease, which is a dangerous cyclic copper corrosion phenomenon induced by the exposure to air of the reactive cuprous chloride [Cu Cl] species located inside the archaeological anklets. Indeed, when cuprous chloride is exposed to the atmospheric humidity cyclically reacts with Oxygen and the water coming from the humid atmosphere thus gives rise to the formation of the greenish atacamite [$Cu2(OH)3Cl$] and its polymorphs, that reacts with copper to form new cuprous chloride and water, in this way copper, chloride, Oxygen and water are converted into cuprite [$Cu2O$] and atacamite [$2Cu2(OH)3Cl$] in a cyclical and continuous process that can disfigure the archaeological objects [14].

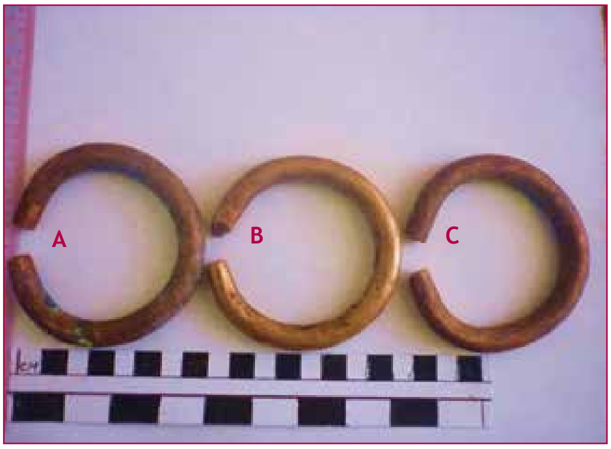

Fig. 12 - Shows the three anklets (the first side) after treatment.

Fig. 13 - Shows the three anklets (the second side) after treatment.

- ME &SEM examinations of the three anklets show the elongation of the bronze grains revealed the use of the hammering method in the Manufacture of the anklets after casting.

- This played a negative role in their deterioration due to the existed strains inside the metallic structure. In addition to the appearance of deterioration spots dispersed on the metal surface represent in Uniform corrosion dispersed on the surface of anklet A , Grieve corrosion and the micro-crocks in the second anklet B, and micro-crocks with pitting corrosion which distort the surface of the third anklet C.

- The study revealed one type of corrosion pattern on the archaeological anklets. It was shown that the structure of the corrosion pattern is closely linked to the type of corrosion process. A phenomenon common to the structure is decupification . It was also shown that the corrosion structure has several features:

- Existing three layers (external , cuprous oxide and internal).

- The external layer due to a more severe dissolution of the alloy associated with the presence of soil elements in the internal layer.
- Relatively large amount of chlorides in the vicinity of the alteration front, which means the occurrence of mass transportation of chlorides from the soil to the metallic phase inward.

- XRF analysis indicated that the anklets were made of bronze alloy [Cu+Sn], tin was found in a high amount in the three anklets ,the percentage of it varied from [14.78%-16.83%], and they had a very low percentage of Lead, Iron and Zinc as purities, these purities contents may came from the used copper ores during extraction. Also we can deduce that the ancient manufacturer recognized that the Lead isn't valid to manufacture the anklets by hammering technique.

- It must be noticed that in the case of artifacts found in archaeological soils, chemical composition and properties (PH, buffer capacity) of soils have been modified with time, and that both climate and a activity on the site have changed. It is obvious that the soil in which the artifacts were discovered cannot be regarded as the initial one in which they were left or buried. Then in order to define a real meaning of an archaeological soil condition regarding the corrosion, it is necessary to consider the soil micromorphology in order to determine the evolutions of the soil characteristics such as decalcification, modification of buffering capacity[15].

- The choice of method for cleaning depends on what is required from the object, what is made of, and what condition it is in. The mechanical cleaning of metals is preferred method for removing disfiguring corrosion, It allows more control and has less effect on the metal alloy. Jedrzejewska [16], suggested to leave small strips of corrosion, untouched by cleaning, in less visible places as evidence of the state of the object before. However, the use of chemical treatments for the anklets is acceptable than the mechanical cleaning as these objects had a thick, hard and crust layers of corrosion products mixed with the dirty of soil, it is very difficult to remove it by mechanical methods with surfaces that can be easily damage, by the pressure exerted during mechanical cleaning, besides the mechanical methods will create new points (pin Holes) for a new corrosion. Also if we leave small strips of corrosion or a thin layer of patina as Jedrzejewska suggested, these strips will become a negative electrode (Cathodic), whereas the metal under it, become anodic, and in existing a moisture as electrolyte, immediately a Galvanic cell will create and the corrosion process will start.

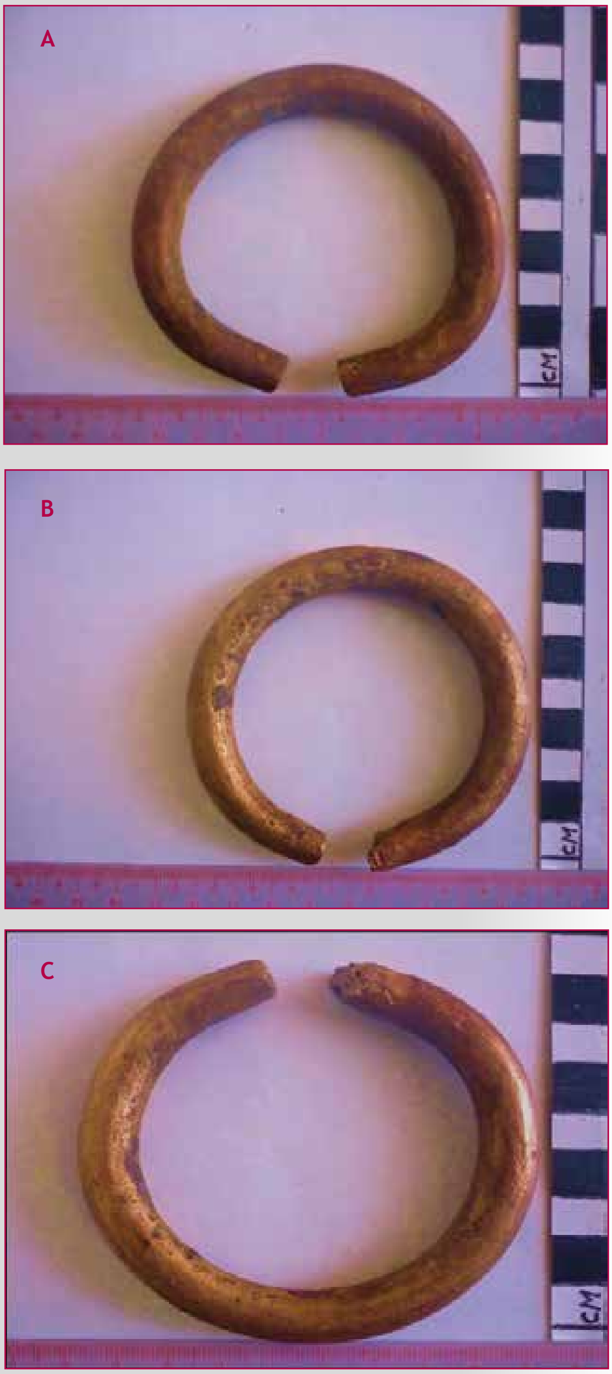

Fig. 14 - Shows the three anklets (A,B,C) after treatment.

CONCLUSIONS

The information that can be derived from mineralogical study of ancient bronzes has a direct impact on the degree to which surface cleaning of such objects can be carried out during conservation. One of the most currently favored and best-informed approaches to their surface cleaning is to examine the object carefully by modern apparatus .

It is necessary to consider the soil micromorphology in order to determine the evolutions of the soil characteristics such as decalcification , modification of buffering capacity.

There is still much to be understood about the chemistry and pH conditions that prevail in bronze objects and lead to an accumulation of cuprous chloride in the corrosion products. The cupric complexes must play an important role in the continued reactions giving rise to bronze disease before either all of the cuprous chloride is consumed or the humidity levels in pits or in zones contiguous with the surface drop below levels required for continuous reaction.

There is a strong interaction between the surrounding environment and alloy, also there is a strong relation between the surrounding medium and structure of corrosion layers.

The choice of method for cleaning depends on what is required from the object, what is made of, and what condition it is in.

Abstract

The aim of this paper is to examine, in detail, the corrosion of the selected objects grown during the long-term burial and identify its products; this will help us to understand the corrosive factors and the degradation mechanisms , as well as to identify their constituting metals in order to carry out scientific treatment and conservation .

For this purpose, samples from the objects were examined by Metallographic Microscope (ME) and Scanning Electron Microscope (SEM), while the corrosion products were analyzed by X-ray diffraction (XRD). X-ray fluorescence(XRF) was used to determine the bulk elements of the objects.

XRD data showed that the corrosion products are cuprite , atacamite and paratacamite , whereas XRF analysis pointed out that the anklets are composed by a bronze alloy. Microscopic examination reveals that the three anklets suffered deterioration mainly in spots. Exploiting the collected info, chemical cleaning was chosen for treating the objects.

Keywords

bronze objects; corrosion; SEM; XRF; XRD; treatment; conservation

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