Abstract: This study aims to gain further insight into the surface features of five leaded bronze from Dhamar museum, Yemen, to know the role of chemical composition in deterioration process, identify the ancient manufacturing processes, which were used to produce the statues, to get a deeper in sight into the morphology and mineralogy of corrosion products, the cause and mechanism of corrosion process to control it and to identify the types of corrosion products of selected objects as well as their constituting metals in order to carry out scientific treatment and conservation to avoid the further deterioration. To achieve that the selected objects have been studied by means of the combined use of metallographic microscope, scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS), X-ray diffraction (XRD) techniques. Metallographic examination results indicated a non-homogenous structure, localized corrosion spots and the existence of lead islands in the alloy; scanning electron microscope examination showed the microstructure for the grains and aspects of deterioration, it confirms metallographic examination results. The chemical composition analysis declared that the statues are made of leaded bronze alloy. The patina of the examined objects were consisted of two layers and composed of Cuprite, Atacamite, Quartz. Finally, obtained results helped us in treatment and conservation the selected objects.

Keywords: Lead Bronze, Chemical Composition, Corrosion Products, ME, SEX&EDX, XRD, Treatment

1. Introduction

Ancient bronze consisted of tin that ranged from about 2% to about 16%. The bronzes containing tin more than 10% are generally harder and more corrosion resistant than either of the pure metal [1].

It has been reported that lead was added to bronze alloy in ancient Egypt during the Greek / Roman period until the percentage of it reached to 32.5% in same statues and coins from that period[2].Although it doesn't mix with the other contents of the alloy but it improves the fluidity of the melted bronze alloy and thus makes easier to machine [3].

The technology of high tin leaded bronze casting for producing mirrors was developed to a high level of sophistication in China during the late Eastern Chou and Han periods (400–200 BC). Romans also used these high-tin Cu based alloys for producing mirrors whose chemical composition and structure were very similar to those used in China. This similarity has suggested that the possibility that the use of these unusual alloys for producing mirrors could have been transmitted to Rome by way of trade with China [4].

Archaeologists have observed that on Chinese and Roman bronze mirrors some areas are not corroded and are still curiously characterized by a reflective and silvery-lustrous surface. The presence of these areas indicate that the mirrors have successfully resisted corrosion for about two millennia and that the original finished surface is still present [5].

To explain this curious feature, some authors have suggested that a glassy amorphous silicate containing tin, iron and some copper is present on the uncorroded surface, which is highly impermeable to corrosive species [6]. Also many studies have been conducted to determine the chemical compositions of several Yemeni Archaeological artifacts. These the majority of the investigated artifacts were made out of leaded bronze and that the lead content varied from about 2% to about 25%.

When exposed to the ambient atmosphere, copper and copper alloys form a thin layer of corrosion. This layer is called patina and appears to be generally brownish-green or greenish-blue. Patinas are chemically and metallurgically complex structures. A large number of studies on ancient and historical soil or the ambient atmosphere for a long time [7, 8, 9].

Archaeological artifacts represent excellent samples for such studies as they are of great importance for scientists and conservators to control and stop the process of deterioration of ancient and historic metals in museums. Numerous studies on ancient and historical bronzes have tried to establish the chemical characteristics and structure of natural patinas grown on artefacts 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 artefact (monuments, large sized statues smaller objects). The corrosion deposits are often complex, stratification of
surface layers, intergranular or transgranular corrosion, etc. have been pointed out. Furthermore most of the published studies have also been carried out in view of improving conservation methods in order to prevent the so-called (bronze disease), a post burial cyclic corrosion phenomenon occurring in the atmosphere, due to the presence of cuprous chloride within the patinas rather than to get a deeper insight into the corrosion behavior of Cu-Sn alloys in natural environments [10-20].

This study aims to know the role of chemical composition in deterioration process, to identify the ancient manufacturing processes, which were used to produce the statues, to get a deeper insight into the morphology and mineralogy of corrosion products, the cause and mechanism of corrosion process to control and stop it, and to identify the types of corrosion products of selected objects as well as their constituting metals in order to carry out scientific treatment and conservation to avoid the further deterioration.

To achieve that the selected objects have been studied by means of the combined use of metallographic microscope, scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS), X-ray diffraction (XRD) techniques.

2. Materials and Methods

The investigations were conducted on five statues of camels, they were discovered by the Yemeni mission in Gabal Al- lawd site, Al-Gawf, Yemen, Season 2002 A.D, and now they are situated in Dhamar regional museum. The statues date back to Minaean Period in Yemen [6th century B.C. to 24 B.C], they were manufactured in a badway, so they haven't accurate dimensions and they can classify as the following:

- The statue no. A, is a solid cast statue for Camel and two men ride it. It's dimensions (5.5 cm length x 5.5 cm height) and it suffered from deterioration factors, covered with a thick layers of black corrosion products mixed with soil dirt's (Fig. no.1A).
- The statue no. B, is a solid cast statue for Camel and a man rides it. It's dimensions (4.6 cm length x 6 cm height); it was suffered from deterioration factors, covered with a thick layer of black corrosion products mixed with soil dirt's (Fig. no.1B).
- The statue no. C, is a solid cast statue for Camel and a man rides it. It's dimensions (5 cm length x 5.4 cm height) and it suffered from deterioration factors, covered with a thick layers of black corrosion products mixed with soil dirt's (Fig. no.1C).
- The statue no. D, is a solid cast statue for Camel and a man rides it. It's dimensions (3.5 cm length x 3.4 cm height) and it suffered from deterioration factors, covered with a thick layers of black corrosion products mixed with soil dirt's (Fig. no.1D).
- The statue no. E, is a solid cast statue for Camel and a man rides it. It's dimensions (3 cm length x 3 cm height) and it suffered from deterioration factors, covered with a thick layers of black corrosion products mixed with soil dirt's (Fig. no.1E).

Figure 1: Shows the statues before the treatment
3. Results

The physical and chemical characterization of the objects was performed by metallographic microscope (ME), scanning electron microscope & energy dispersive spectrometry (SEM & EDS) and x-ray diffraction (XRD). ME was used to show the microstructure of the metal and aspects of deterioration which spread on the metal surface. SEM & EDS was used to more actually examination for the statues and to determine the chemical composition of the statues and X-Ray Diffraction analysis was used to investigate the corrosion products, it can provide valuable information related to the burial condition of the statues as well as the composition of the metal or the alloy.

3.1 Metallographic Microscope Examination (ME)

Metallographic examinations for samples of the statues were performed to show the microstructure of the metal and aspects of deterioration which spread on the metal surface [figs. no. 3 - 6].

Figure 3: ME ex., for a sample from the Camel no. A shows the lead globules dispersed in the alloy

Figure 4: ME ex., for a sample from the Camel no. B shows the lead globules in the alloy and the cracks dispersed in the alloy.

Figure 5: ME ex., for a sample from the Camel no. C shows the pitting corrosion and disturbing of the surface of the alloy

Figure 6: ME ex., for a sample from the Camel no. E shows the lead globules dispersed in the alloy and pitting
corrosion disturbing the surface of the alloy.

3.2 Scanning Electron Microscope Examination and Energy Dispersive Spectrometry (SEM&EDS)

SEM&EDS examination showed the microstructure, the appearance of deterioration spots and the chemical composition of the statues analyzed by using an Inspect S 50 (FEI), the obtained examination Photos are given in [figs.7,8,9,10,11], Scans and the identified elements are given in [figs.12,13 A, B and tables 1, 2].

Figure 7: SEM ex., for a crossed section of the Camel no. A shows lead globules (lighter areas), cracks and distorting alloy (3000x).

Figure 8: SEM ex., for a crossed section of the Camel no. B shows the Crevice corrosion and cracks (400x).

Figure 9: SEM ex., for a crossed section of the Camel no. C shows Pb globules (lighter areas), cracks and distorting of the edge of the alloy (1500x).

Figure 10: SEM ex., for a crossed section of the Camel no. D shows Pb globules (lighter areas), pitting corr., cracks and distorting the edge of the alloy (1500x).

Figure 11: SEM ex., for a crossed section of the Camel no. E shows Pb globules (lighter areas), pitting Corr., and distorting of the edge (1500x).
Figure 12: A, B shows SEM&EDS ex., of the Camel no. A, photo A shows the consist of the alloy, lead globules (lighter areas) dispersed in the alloy and B shows SEM&EDS Scan for the elemental composition of the Camel no. A.

Table 1: Shows the chemical composition of the Camel no. A.

<table>
<thead>
<tr>
<th>El</th>
<th>AN</th>
<th>Series</th>
<th>unn. [wt.%]</th>
<th>C norm. [wt.%]</th>
<th>C Atom. [at.%]</th>
<th>C Error [wt.%]</th>
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<tbody>
<tr>
<td>Cu</td>
<td>29</td>
<td>K-series</td>
<td>72.91</td>
<td>81.56</td>
<td>83.46</td>
<td>2.0</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>L-series</td>
<td>7.44</td>
<td>8.32</td>
<td>2.61</td>
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</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>L-series</td>
<td>6.91</td>
<td>7.73</td>
<td>4.23</td>
<td>0.2</td>
</tr>
<tr>
<td>O</td>
<td>8</td>
<td>K-series</td>
<td>2.13</td>
<td>2.39</td>
<td>9.70</td>
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<td></td>
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</tbody>
</table>

Figure 13: A, B shows SEM&EDS ex., of the Camel no. D, photo A shows the consists of the alloy lead globules (lighter areas) dispersed in the alloy and B shows SEM &EDS Scan for the elemental composition of the Camel no. D.

Table 2: Shows the chemical composition of the Camel no. D

<table>
<thead>
<tr>
<th>El</th>
<th>AN</th>
<th>Series</th>
<th>unn.[wt.%]</th>
<th>C norm.[wt.%]</th>
<th>C Atom.[at.%]</th>
<th>C Error [wt.%]</th>
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<td>80.68</td>
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<tr>
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<td>2.31</td>
<td>9.36</td>
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<tr>
<td>Cl</td>
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<td></td>
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<td>Total:</td>
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<td>100.00</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

3.3 X-Ray Diffraction Analysis (XRD)

X-Ray diffraction analysis was carried out for corrosion product samples were taken from the surface of each object, by using A Philips X-Ray, Diffractometer type: pw1840 with Cu k& Radiation.

The obtained diffraction scan given in figs. no.[13, 14,15] and the identified compounds represented in the table[3].
Figure 14: shows XRD scan for the corrosion products of the Camel no. A.

Figure 15: shows XRD scan for the corrosion products of the Camel no. C.

Figure 16: shows XRD scan for the corrosion products of the Camel no. E.
Table 3: shows XRD analysis results of corrosion products of the statues.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Major</th>
<th>Minor</th>
<th>Traces</th>
</tr>
</thead>
<tbody>
<tr>
<td>The statue no. A</td>
<td>Cuprite (Cu₂O)</td>
<td>Quartz (SiO₂)</td>
<td>Gaylussite (Na₂Ca(CO₃)₅H₂O)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atacanmite (Cu₂(OH)₃Cl)</td>
<td>Botallackite (Cu₂Cl(OH)₃)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tephroite Mn₂SiO₄</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lead Oxide (Pb₂O)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tin Oxide (SnO)</td>
<td></td>
</tr>
<tr>
<td>The statue no. C</td>
<td>Cuprite (Cu₂O)</td>
<td>Piastite FeO</td>
<td>Mullite (Al₆Si₂O₁₃)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calcite (CaCO₃)</td>
<td>Cassiterite (Sn₂O)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Atacanmite (Cu₂(OH)₃Cl)</td>
<td>Vashegyite (Al₄(PO₄)₄(OH)₃·XH₂O)</td>
</tr>
<tr>
<td>The statue no. E</td>
<td>Atacanmite (Cu₂(OH)₃Cl)</td>
<td>Geothite (Fe OOH)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tephroite (Mn₃SiO₄)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tin Chloride Hydroxide (SnCl₄·5H₂O)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lead Oxide (Pb₂O)</td>
<td></td>
</tr>
</tbody>
</table>

3.4 Treatment and conservation of the statues

According to the obtained examination results the statues have a good metallic state, but they are covered with thick layers of corrosion products, chemical treatment was chosen assisted by skilled mechanical cleaning, this helped us to reveal and discover the original surface topography.

The treatment procedures included the following steps:
- Soaking the statues completely in dilute solution of Calgon [Sodium Hexametaphosphate Na(PO₃)₆], that was changed many times assisted by gentle mechanical cleaning with silk brush from time to time to dissolve the corrosion layers and the calcareous sediments. This step succeeded in removing the calcareous sediments and left a red/black layer covering the surfaces.
- To dissolve and remove the oxides layer [Cuprite Cu₂O and Tenorite CuO], 3% solution of Sulphuric acid/H₂SO₄ was used assisted by a brush to remove the loosened layer, this was done with regular checks and removing loosened layer, these procedures succeeded in removing all the corrosion products.
- After that the statues were soaked in water and washed by a tooth brush to dislodge residue from crevices.
- Repeated washing in hot deionized water baths with altering heating and cooling to ensure flushing capillaries to remove any chemical residues.
- Drying in repeated baths of ether and ethanol followed by drying in hot sawdust and mopped dry with soft, clean cloth.
- Finally the statues were isolated with paraloid B-72 dissolved in acetone 3% by using a brush Figs. no. [17, 18, 19].
4. Discussion

The investigation results indicated that the majority of the investigated statues were made of leaded bronze and that the Lead content varied from about 8.19% to 8.32% and also a high amount of Tin ranged from 7.73% to 8.00%. Tylecate [21] mentioned that the cost of Pb bronze alloy is low with respect to more expansive and rarer Tin, therefore, the use of Pb bronze is justified from an economic point of view. But in the current study the examination and analysis of the selected statues indicated that the statues had a high amount of Lead and Tin.

The study have proceeded new insights concerning the identification of component materials of the leaded bronze artifacts characteristic of ancient Yemeni metallic objects, the addition of Lead to bronze alloy has many advantages in spite of the fact that it decreases the bronze mechanical properties as well as the fear of enhanced selected corrosion or galvanic corrosion. Lead is heavier in weight than Tin or Copper and consequently will lead to more stability of the bronze statues especially for large size statues. Lead is also cheaper than tin or copper this will lead to cheaper production of large objects. In addition leaded bronze alloy doesn't have interior corrosion resistance than normal bronze alloy, when exposed to moist air or mild soil, as the presence of Lead will produce protective coating or insulting coating. In other words, under such conditions, the presence of Lead in the bronze alloy has a positive effect or an advantage. Also the study showed that the ancient Yemeni manufacturer knew lost-wax casting to manufacture the statues. In solid cast, the manufacturer was started by making a full-sized model of the statue using wax and make all the details in it, then covering the wax model with clay to make the exterior mold and making two holes, one in the top and the other in the bottom of the clay mold, then the mold was left to dry and heated in a kiln until it transfers to a fired mold and the wax runs out through the holes and leaves the fired mold contents the figures and details of the statue stamping inside it. After that the manufacturer closed the bottom hole and filled the liquid metal or alloy from the top hole. When the metal has cooled, the external mold was chipped away, revealing the metallic statue, finally the manufacturer polishes it, shows the features and makes the fine details.

Ingo[22] studied the surface microchemical structure of high tin leaded bronze Roman mirrors by means of scanning electron microscopy combined with energy dispersive spectrometry (SEM-EDS),X-ray diffraction (XRD) and optical microscopy (OM) techniques. The results allowed understanding of the origin of their high chemical stability and silvery-lustrous appearance. Indeed, some areas of the selected Roman mirrors are still characterized by a highly reflective and silver colored surface even though they have been buried in the soil for about 2000 years. The micro-chemical results obtained
from these areas have revealed that the mirror surface was tin enriched via inverse-segregation phenomenon by tailoring the cooling parameters. Furthermore, the presence of tin could be likely enhanced via cycles of oxidation and selective copper corrosion processes, thus resulting in a tin surface enrichment as a semi-transparent amorphous-like tin oxide (SnO) film, as well as a copper depletion at the outer surfaces [23–27].

In this investigation, five leaded bronze statues excavated during the excavation of Yemeni mission in Gabal Al-lawd site, Al-Gawf, Yemen, Season 2002 A.D. The degree of deterioration was determined for all statues by means of visual inspection. It was based on an estimation of corrosion depth, surface condition and the part of the cross-section converted into corrosion products. A small fragment from each statues was analyzed by using metallographic microscopy and scanning electron microscopy combined with energy dispersive spectrometry (SEM&EDS). All statues had a large content of copper, and two of the alloying metals such as tin and lead, also with some traces from Oxygen and Chloride. The objects displayed a large variation in metal composition, probably due to assiduous recycling of metal. Some analytical results are presented in (Table 1,2). The corrosion products were analyzed by X-ray diffraction (XRD). A list of identified corrosion products is shown in (Table 3). Naturally, the corrosion products are dependent on water-soluble salts in the soil. Inversely, the surrounding soil has been enriched in copper and other metals from the deteriorating object. As shown in Table 3, cuprite was dominating among the corrosion products. The most frequent copper hydroxide salt was Atacamite, formed through reaction between the statues and Chlorine Ion in the soil. The concentration of chlorine in the statues was in a range of 0.82 to 1.50%. A high Lead and Tin contents in the object were reflected by Lead Oxide (PbO), Tin Oxide(SnO) and Tin Chloride Hydroxide (SnCl4. 5H2O) in the corrosion products. When Cu-based alloys are exposed to soil containing aggressive ions, greenish colored corrosion products are mainly formed on the surface, it is commonly known as patina, it was usually composed mainly of cuprite as the first layer formed on the surface of the objects and basic copper chloride [Atacamite, Paratacamite….etc...], depending on the content of environment [water, chlorides, sulfates, carbonates, ammonia…..etc...]. corrosion process can take a long time as happened on copper base artifacts. The constant presence of chloride in the soil is responsible for the so-called [bronze disease]. Furthermore, the bulk alloy structure of these bronze statues clearly indicates the presence of as cast dendritic structures that can be preferentially attacked by aggressive agents.

SEM & EDS analyses showed Anon homogeneoue us alloy can be observed for statues, a localized corrosion and apart from some small grains and islands, formed principally by Cu, Sn and Pb (lighter areas) (Figs 7-11,12A,13A). It is important to notice that in many areas we found the presence of Sn( as it shown in Figs.8, 10, 11), Sn was present in a small and thin layer. Furthermore, the ME images also reveal the presence of islands of lead dispersed in the alloy. These results indicate that the statues were produced by using leaded bronze alloys. In spite of this condition, the Galvanic corrosion tendency when the alloy is exposed to moist air or soil isn’t possible as lead compound are electrically insulating.

X-Ray diffraction analysis of the corrosion products of statues (Figs.14,15,16 and table 3), revealed the presence of different minerals including Cuprite, Atacamite, Quartz, Tephroite, Lead Oxide, Tin Oxide, Piustite, Calcite, Goethite, Tephroite, Tin Chloride Hydroxide and traces from Gaylussite, Botallackite, Mullite and Vashegyite. The presence of Cuprite (Cu2O) is due to selective corrosion of the main alloying element, which is re-deposited after dissolution onto the surface of the objects, thus forming a copper enriched layer. The presence of basic copper chloride is related to the sandy and saline nature of the Soil, whereas the statues were buried. It played an important role in their severe corrosion, this soil which is porous and changed from Sub-saturation to saturation with water, had different salt ions, specially the dangerous chlorine ion, this circulation of saline water in the soil had a serious effect on the objects. The presence of Lead Oxide, Tin Oxide and Tin Chloride Hydroxide reflected the chemical composition of the statues and indicated that there is a strong relation between the chemical composition of the alloy and the kind of corrosion products. Multivariate analysis, taking into account the objects and soil properties, on the one hand; and the environmental parameters as a whole, on the other. The influence of the soil grain size agrees with the electrochemical theory of metal corrosion. It is generally accepted (e.g., [28]) that corrosion of metals in soil occurs through the activity of electrochemical corrosion cells and, hence, two factors are essential: the supply of an oxidizing agent (usually oxygen from the air) and the presence of an electrolyte (usually, a water solution). Accordingly, a moderately well aerated and moist soil, such as sand above the ground water table, should promote corrosion of metals, giving access for oxygen at the same time as the pores are partly filled with water [29]. On the other hand, a fine-grained soil like clay or a coarse-grained soil like gravel or pebble should be less harmful, because, in principle, only one of the two essential factors affects the object. Consistently, Geilmann [30] has shown that bronze objects are attacked by corrosion in well-aerated sandy soils, while a poorly aerated wet boggy soil has, by contrast, a preserving effect.

The presence of Calcite (CaCO3) in the analysis results of Camel statue no. C (Fig.14,Table 2) corrosion products is most probably formed by the reaction of soluble calcium bicarbonate with hydroxide ions produced in the Cathodic reaction of Oxygen, indicated that the soil usually has high Carbon dioxide contents and may be chemically very aggressive because the Carbon dioxide may react with water to form Carbonic acid, which may attack metals directly and prevent the formation of a protective film surface. A calcareous soil may also act in a quite benign, however, especially if Carbon dioxide and water produce the soluble Calcium bicarbonate. This may act to protect the objects from corrosion, since Calcium bicarbonate is a salt of a weak acid, its aqueous solution is very alkaline.
and by binding with Carbon dioxide, it prevents the extensive dissolution of Copper (1) ions. At values of pH >8 Calcium Carbonate precipitates as Carbonate, and in subsequent acidic condition, this may dissolve instead of Copper(11) compound, the overall PH in dilute natural ground water is principally controlled by this Ca CO₃-H₂O-CO₂ equilibrium.

The existence of Piustite Fe O and Geothite( Fe OOH) in a minor amounts in corrosion products of the statues no. C, E(Figs. 15,16 and Table 3), may be as a result of migration of Iron corrosion from adjacent iron objects to the selected leaded bronze statues in the burial environment or from the buried environment itself as it is very rich with Iron compounds, this indicates the strong interaction between soil components and corrosion products.

5. Conclusion

- The combined used of ME, SEM-EDS and XRD analytical techniques have provided good insight into the bulk nature and surface corrosion products grown on the objects during the archaeological burial.
- The statues are made of a ternary alloy, composed of copper, tin and lead, with fusion defects. The Sn content lies between 7.73% and 8.00% in weight, lead ranges from 8.19%-8.32%. We can deduced the following:--
  1) The alloy is not completely homogeneous.
  2) The existences of lead in the alloy formed a black protected layer on the surfaces of the statues and protect it from further and more dangerous corrosion. Also the existence of lead in islands dispersed in the alloy may be caused a serious damage for the statues.
  3) It seems that Pb bronze alloy was used extensively in various other applications than statues, so more studies are needed to carry out systematic non-destructive characterization of ancient leaded bronze artifacts in Yemen.
- The study showed that the morphology of the surfaces and the elemental compositions of the corrosion products depend strongly on the chemical composition of the alloys. As well as there are a strong relationship between the surrounding environment and the kind of corrosion products.
- The study indicates that soil conditions allowing access for air and water to the object at the same time increases the corrosivity, because the soil where the statues were found is a sandy soil, conditions will be especially corrosive for metals in soil within an area just above the ground water table (where the soil pores are partly filled with water). The extension of the corrosive soil zone will depend on the grain size distribution among the soil particles, which affects the capillary rise of the ground water and also the hydraulic flow through the soil.

References

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