

## ASSESSMENT OF SOME Ag-BASED COINS FROM AYYUBID PERIOD, YEMEN. CORROSION AND METHODS OF TREATMENT

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### Abstract

*Some Archaeological Coins have been discovered in Al- Banawa excavation, Dhamar, season 2002, and now they are situated in Dhamar museum, Yemen. These coins suffered from corrosion products mixed with particulars of the soil and others deterioration aspects. This work aims to evaluate the effectiveness of the corrosion mechanism on the coins, identify the morphology and mineralogy of corrosion products and identify the Metallic composition of these Coins and the best methods for treatment. To achieve these aims analytical and characterization study on areal samples from the coins were performed using metallographic microscope, scanning electron microscope, X-Ray Diffraction Analysis and X-Ray Florence. The examinations showed the degradations and deteriorations of the coins, processes that started in the burial time. X-ray fluorescence results showed that the coins consists of ternary alloy [ Silver, Copper, Lead ]. The difference in potential between the three metals in the Coins play a serious role in the corrosion process. Finally, the results obtained helps in choosing the best methods of treatment and conservation.*

**Keywords:** Islamic coins; Ag-based alloys; Corrosion mechanism; XRD; SEM; XRF; Conservation.

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### Introduction

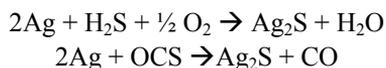
In 1173 AD (569 A.H), the brother of Salah al-Din (Saladin), Turanshah lead an expedition into Yemen to conquer it for the newly established Ayyubid family domains. Turanshah captured Sana'a after he had already conquered the whole of the western and southern part of the country, but it was soon recaptured by the Sultan of Hamdan. It was another of Salah al-Din's brother, Tughtakin, who consolidated Ayyubids power in Yemen and in 1189 AD (585 AH), finally established Sana'a as his capital. Upon the Ayyubids, departure to rule from Ta'izz in the south, the city was captured by a large farce of tribesmen supporting the Zaydi Imam. Although it was recaptured by the Ayyubids a few years later, Sana'a was to be for some decades a bone of contention between the Ayyubids and Zaydis, frequently changing hands and experiencing a period of great uncertainty and continual warfare. This was eventually resolved by the rise of Rasulids as successors to Ayyubids and the certain of a new Rasulid state in 1228 A.D (628 A.H).

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In August 2002 A.D, the Yemeni mission of Antiquities discovered in El-Banawa site, Dhamar governorate, Yemen, a big group of silver coins written in Arabic inscriptions and it dates back to Ayyubid period in Yemen [569 - 628 A.H]. Seven of these coins were selected to study; they suffered badly under the influence of degradation factors .

Silver and many of its alloys are easily tarnished at exposure to the environment. Tarnishing is due to the reaction between Silver and Hydrogen Sulfide (H<sub>2</sub>S), carbonyl sulfide (OCS), or various other sulfur-containing organic compounds in the atmosphere to form silver sulfide according to the following simplified overall reactions:



The rates of these reactions are strongly dependent on temperature, concentration, and relative humidity. In the case of sterling silver, the tarnished layer contains cuprous sulfide (Cu<sub>2</sub>S), which may be distributed in homogeneously depending on the composition and distribution of the silver-copper phases in the alloy [1-3].

Furthermore, the Ag or Au based alloys can be characterized by different amount of impurities coming from the extractive or refining processes, which can influence on the long-term mechanical and chemical properties [4]. The contact between silver and copper in the silver copper alloy coins has enhanced the corrosion phenomenon whose main agent is the chloride anion coming from the soil, this induces the formation of silver and Cu(I) chlorides that could give rise to the copper cyclic reaction that continues to corrode copper when exposed to oxygen and humidity, where there are two detected basic copper chlorides: atacamite and paratacamite that are identical in chemical composition but differing in crystal form the second one is found as a powdery, light green secondary corrosion layer on the patina surface, while the first one, atacamite occurs as a sugary-looking coating of dark green glistening crystals [5]. Often this dark green crystalline atacamite is altered to a paler green powdery product of paratacamite [6, 7]. The soluble chlorides in the presence of copper or its salts in contact with silver as silver plated copper objects or as an alloy of the two metals will corrode silver severely resulting in occurrence of insoluble thick layer of silver chloride [8].

This study aims to:

- Know the history and mint place of the coins.
- Obtain new information about the manufacture technologies used to make the coins and the provenance of the metal, metallurgical (microstructural) or elemental composition.
- Show the evolution of copper and lead contents of the coins.
- Identify the metallic composition of the coins and explain its relation with the economic situation of that period.
- Investigate the nature of corrosion grown during the long-term burial and identify its products that will help us understand the corrosive factors and the degradation mechanisms.
- Cleaning the group of coins from the superficial dirt and the corrosion products in order to discover as much as possible the surface topography, and to reveal the surfaces details.
- Stabilize the coins against further deterioration.

This was achieved through a systematic study for the group of coins using Metallographic Microscopy, Scanning Electron Microscopy, X-Ray Diffraction and X-Ray Fluorescence.

## Materials and Methods

The coins are only Islamic currency, written with Arabic inscriptions. They are classified as the following:

- The first group no. D, consists of three coins no. 1, 2, 3; the diameter of the coins 2.2cm and 1mm thick (Fig. 1).
- The second group no. E, consists of four coins no. 4, 5, 6, 7; the diameter of the coins ranges from 2.2 - 2.4cm and 1mm thick (Fig. 2).

The deteriorations and degradations that these coins endured can be presented as follows:

- All the coins have a thick black layer of corrosion residue that changed their appearance (figs. 1 and 2).
- Two coins no. 6 and 7 have a thick black layer of corrosion mixed with soil particulars that changed their appearance (fig. 2).
- Three coins no. 2, 3, 4 have some micro cracks.
- One coin no. 3 has a thick black layer of corrosion mixed with soil particulars changed their appearance and lead it to fracture (fig. 1).
- Five coins no. 2, 3, 4, 5, 6, 7 are missing fractured pieces and others lost their circular form (Fig. 1 and 2).



**Fig. 1.** The obverse and reverse of coins before treatment: a – coin 1, b – coin 2, c – coin 3



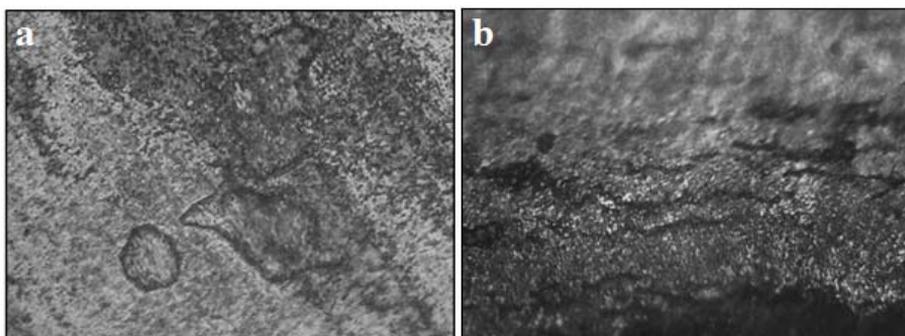
**Fig. 2.** The obverse and reverse of coins before treatment: a – coin 4, b – coin 5, c – coin 6, d – coin 7

## Results

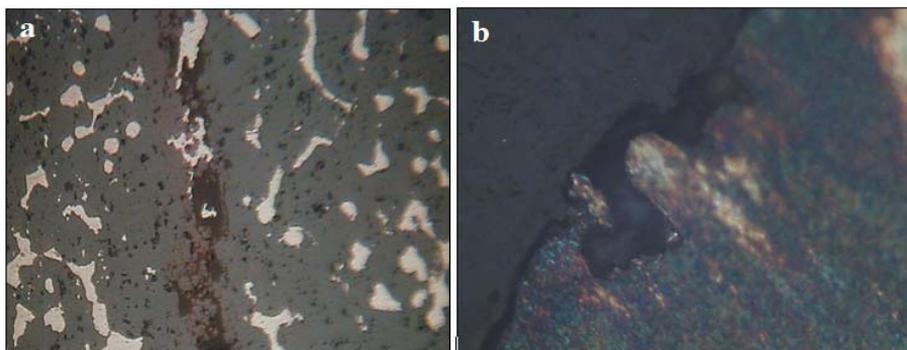
A series of examinations and analyses of the samples taken from the coins, were performed by modern techniques, as the following:

### *Metallographic Microscope Examination (ME)*

A thorough examination and photography of the coins was performed with the metallographic microscope in order to show the structure of the coins, highlighted the degradations and deteriorations of the coins, and processes that started in the burial time, due to different corrosion factors (figs. 3, 4 and 5).



**Fig. 3.** Micrograph of samples (150X): a – coin 1 with the micro cracks and the lead islands dispersed in the alloy, b – coin 3 with micro cracks dispersed on the surface of the alloy.



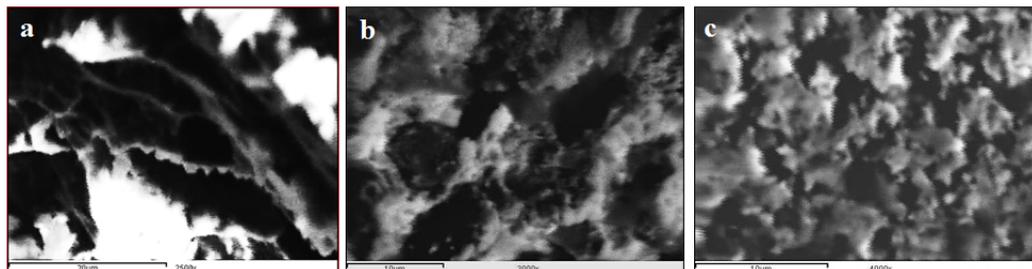
**Fig. 4.** Micrograph of samples (150X): a – coin 4 with crevices of corrosion, b – coin 6 with corrosion crevices dispersed on the edge of the coin.



**Fig. 5.** Micrograph of a sample from the coin no.7 shows a block of lead in the alloy and the elongation of grains (150X).

### Scanning Electron Microscope Examination (SEM)

SEM examination showed the microstructure of the coins, in addition to the appearance of deterioration spots, as it is shown in figure 6.



**Fig. 6.** SEM images of samples from coins: a – coin 1 – crevice corrosion and distorting of the structure (2500X), b – coin 4 – intergranular corrosion (3000X), c – coin 7 pitting corrosion (4000X)

### X-Ray diffraction Analysis

Samples from corrosion products were analyzed by using a Philips X-ray Diffractometer with Cu  $K\alpha$  radiation. The aim of this analysis is the identification of the corrosion compounds in order to decide whether it is authentic, stable and suited to certain kinds of conservation treatment. This information can help in choosing the best environment for coins in storage or in show-cases. The obtained diffraction-scan given in figure 7 and the identified compounds represented in table 1.

**Table 1.** XRD results of corrosion products of the coins.

Samples	Compounds		
	Major	Minor	Traces
The coin no.1	Silver Ag	Domeykite ( $AsCu_3$ ) Topazplite( $3CaO \cdot Fe_2O_3 \cdot 3SiO_2$ ) Brushite( $CaPO_3(OH) \cdot 2H_2O$ ) Silver Cyanide ( $AgOCN$ )	Iron Chloride Hydrate ( $FeCl_3 \cdot H_2O$ ) Chlorargyrite ( $AgCl$ ) Lead Oxide ( $Pb_2O$ ) Lime ( $CaO$ ) Tenorite ( $CuO$ )
The coin no.3	Chlorargyrite ( $AgCl$ )	Malachite ( $Cu_2CO_3(OH)_2$ ) Paratacamite ( $Cu_2(OH)_3Cl$ ) Tephroite ( $Mn_2SiO_4$ )	Tenorite ( $CuO$ )
The coin no.5	Chlorargyrite ( $AgCl$ )	Sodium Oxide ( $Na_2O$ ) Atacamite $Cu_2(OH)_3Cl$ Paratacamite ( $Cu_2(OH)_3Cl$ ) Cuprite ( $Cu_2O$ )	Orthoclase( $KAlSi_3O_8$ ) Topazplite ( $3CaO \cdot Fe_2O_3 \cdot 3SiO_2$ )
The coin no.7	Quartz ( $SiO_2$ ) Orthoclase ( $KAlSi_3O_8$ )	Domeykite ( $AsCu_3$ ) Copper Zinc ( $CuZn$ )	Atacamite $Cu_2(OH)_3Cl$ Sodium Oxide ( $Na_2O$ ) Chlorargyrite ( $AgCl$ )

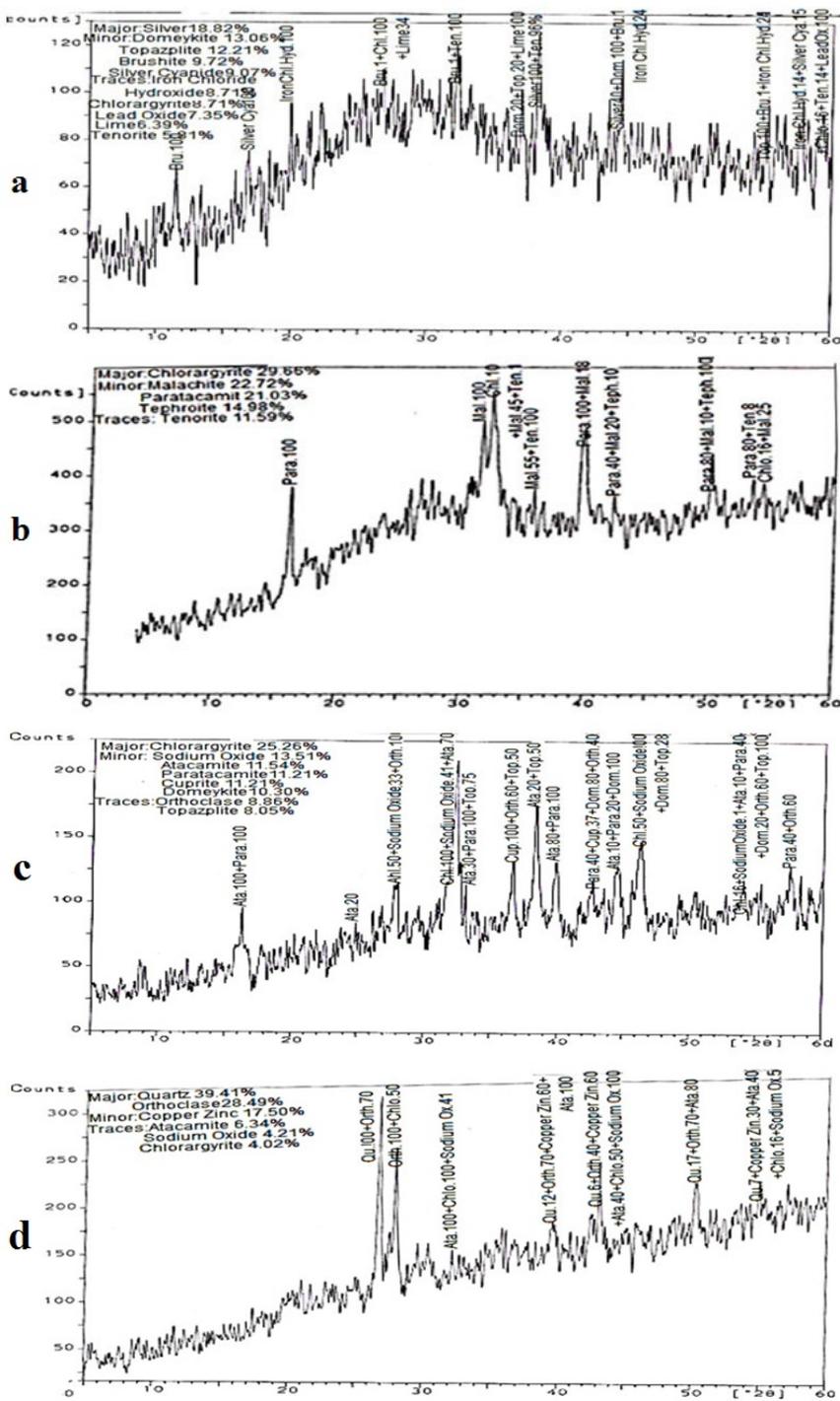


Fig. 7. XRD pattern for the corrosion products of the coins: a – coin 1, b – coin 3, c – coin 5, d – coin 7

***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, the coins were analyzed by this technique to determine their composition, by using NITON/XL8138 (USA), driven with a software version 4.2E. The results are shown in the table 2.

**Table 2.** shows XRF analysis results of the coins

Element/Sample	Ag	Cu	Pb	Zn	Sn	Fe	Mn
Coin 1	69.13	13.50	14.42	1.62	0.17	1.16	-
Coin 4	68.38	14.18	13.40	1.13	1.05	1.24	0.62
Coin 7	70.18	13.95	11.60	2.38	0.47	0.45	0.97

***Treatment and Conservation***

The mechanical cleaning of metals is the preferred method for removing disfiguring corrosion. It allows more control and has less effect on the metal alloy. However, for coins where the main aim is to reveal as much detail as possible, the use of chemical treatment is preferable than the mechanical cleaning, as these coins are often thin and brittle with surfaces that can be easily scratched or marked, even a very gentle pressure exerted during mechanical cleaning can damage them. The chemical treatment was chosen and assisted by skilled mechanical cleaning, this helped us to reveal and discover the original surface topography.

Sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) was selected for treatment of the coins, as it was found that it is the least damaging and fastest acting solution, most of the others reagents are capable of harming the sterling silver alloy.



**Fig. 8.** The obverse and reverse of coins after treatment: a – coin 1, b – coin 2, c – coin 3

The treatment procedures included the following steps:

- Two coins no. 6, 7 were soaked in alkaline Rochelle solution that was changed many times, assisted by gentle mechanical cleaning with brass scratch brushes and hard nylon tooth-brush from time to time to dissolving the corrosion layer of copper (II) compounds. This step succeeded in removing green copper corrosion products and left a thin black layer covering the coins surfaces.

- All the coins (1–7) were soaked in aqueous 15% sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) for a short time, the corrosion products were removed mechanically with nylon soft brush.
- Rinsing with distilled water.
- Repeated washing in hot deionized water bathes with altering, heating and cooling to ensure flushing capillaries to remove any chemical residues.
- Drying in repeated bathes of each coin, was followed by drying in hot saw dust and mopped dry with a soft and clean cloth.
- The two parts of the coin no. 3 were glued together using Araldite resin.
- Finally the coins were coated with 3% paraloid B-72 solution, dissolved in acetone (Figs. 8 and 9).



Fig. 9. The obverse and reverse of coins 4, 5, 6 and 7 after treatment

## Discussions

By studying the structure and constitution of the grains and phases of these coins, an understanding not only of the properties of a particular metal but also the history of its manufacture may result. For instance, the metallographic investigation serves in revealing the nature of ancient technology of the objects, the manufacturing process consisted of hammering between an immobile and a mobile die of a heated silver alloy blank to make its figures and inscriptions.

Metallographic examination of a sample from the coin no. 3 showed that the coin suffered from stress corrosion, this term is used to describe cracks in some metals as a result of common pressure for each of the mechanical fatigue and the corroded medium (union expansion pressure or internal tension and corrosion reactions), where some cracks are created and then spread in vertical direction of pressure, this occurs in alloys, which is exposed to changes in temperature and fatigues that occur for metal during its formulation, welding, thermal treatments or hammering process.

SEM examination of a sample from the coin no. 4 (Fig. 6b), shows that it suffered from inter granules corrosion, this kind of corrosion is a non-uniform corrosion occurs on the outer boundaries of the grain and happens when the grain boundaries have an energy content higher than its center, the difference in potential between the two locations leads to create a Galvanic cell and finally it could lead to the corrosion of the metal.

X-ray diffraction data showed that the composition of the corrosion product encrustations is chlorargyrite, cuprite, paratacamite, atacamite, quartz, orthoclase and a small amount of silver cyanide, copper zinc, sodium oxide, tephroite, malachite with traces of tenorite, lead oxide, halite. Chlorargyrite is the most familiar alteration products of silver during burial in salty archaeological soils [9-11], paratacamite and atacamite are basic copper chloride, it is

indicated that the burial soil was salty and the coins stayed in ion chloride medium, this corrosion factor played an important role in the deterioration process; the presence of sodium oxide and halite in XRD, confirms the corrosion products [12-18].

The presence of cuprite  $\text{Cu}_2\text{O}$  (Fig. 7) is due to selective corrosion of the main alloying elements, which is re-deposited after dissolution onto the surface of the silver coins, thus forming a copper enriched layer. Furthermore, some cracks are present along the patina as result of volume changes upon corrosion, which enhances the diffusion of soil elements from the soil to the inner areas of the coins. It is presumed that malachite is formed by contact with water from the soil or condensed water charged with carbon dioxide or carbonic acid. Where the first product to form adjacent to the metal is cuprite, malachite usually forms over this cuprite layer [19-23].

The existence of silver cyanide in corrosion products (Fig. 7) probably cyanide, came from the first extraction of silver from its ore, by using sodium or potassium cyanide, the coins were originally made from sulphuric ores.

The existence of iron chloride hydrate  $\text{Fe Cl}_3 \cdot \text{H}_2\text{O}$ , in corrosion products (Fig. 7) may be a result of migration of iron corrosion products from adjacent iron objects to the coins in the burial environment, or from the soil itself, also it indicates that the soil where these coins were buried, is an aerobic soil and has a high level of soluble salts especially chloride salts.

The chemical composition of the coins is listed in table no.2, silver is the main component of all the coins that can be assigned to the class of Ag-based alloy, where the Cu content ranges from 13.50 – 14.18% and the Pb content ranges from 11.60% – 14.42%. Also a very low percentage of Zn, Sn, Fe and Mn is shown. The impurities contents may come from the first extraction of silver from its ore. As a consequence of the intimate content between copper, lead and silver which have different electrochemical potentials, corrosion processes are induced on a microscopic scale. Indeed, the content induces the less noble metal to become anodic in areas where are strongly conductive to corrosion and a preferential dissolution of copper occurs in the less noble anodic areas. The amount of current that flows and therefore, the extent of the corrosion is subject to many variables, among which are the chemical – physical parameters of the burial context, the presence and nature of the electrolyte and the micro-chemical structure of the alloy [5].

As clearly shown by the above reported results, the contact between silver and copper in the silver copper alloy coins has enhanced the corrosion phenomenon whose main agent is the chloride anion coming from the soil. This induces the formation of silver and Cu (I) chlorides that could rise the copper cyclic reaction that continues to corrode Copper, when exposed to oxygen and humidity, where there are two detected basic copper chlorides atacamite and paratacamite that are identical in chemical composition but different in crystal form. The second one is found as a powdery, light green secondary corrosion layer on the patina surface, while the first one atacamite occurs as a sugary-looking coating of dark green glistening crystals. Often this dark green crystalline, atacamite is altered to a paler green powdery product of paratacamite [6, 7].

After treatment and conservation, the coins, their figures and inscriptions that could be identified, shows that, the group of coins dates back to Ayyubid period in Yemen (569- 628 AD), they are purely Islamic currencies written with Arabic inscriptions. These coins are classified as following:

- The coin no.1 dates back to the region of the Ayyubid king Al Adal Abu Bakar, on the face (observe) of the coin is written: “Allah, No God but Allah, Mohamed is the messenger of Allah, Al-Amam Al-Nasser ledeen Allah Ahmed Amar Al-Mamanen, minted in Taiz 620 A.H”, on the back (reverse) is written “The name of Allah, Al-king Al-Adal Abu Bakar, the descendant of Al-king Al-Kamal Mohamed the descendant of Al-King Al-Massoud Youssef”, see figure 8.

- Two coins no. 2, 3 date back to the region of the Ayyubid king Tughtakin, brother of Salah al-Din in Yemen, on the face of coins (observe), is written the message of uniformity in the center: “No God but Allah, Mohamed is the messenger of Allah, Allah pray upon him”, in the outer margin is written “name of Allah, El-Nasser king Tughtakin, minted in Damlah 600 A.H” and on the back (reverse) is written “The name of Allah, Al-king Al-Adal Abu Bakar, the descendant of Al-king Al-Kamal Mohamed the descendant of Al-King Al-Massoud Youssef”, see figure 8.
- The coin no. 4 dates back to the region of the Ayyubid king Al-Kamal, on the face (observe) is written “Allah, No God but Allah, Mohamed is the messenger of Allah, Al-Mansour Al-Mastanser Ballah Amar Al-Mamanen, Minted in Aden 600 A.H” and on the back (reverse) is written “The name of Allah, Al king Al-Kamal Abu Al-Maalai Mohamed ibn Al-king Al Adal Abu-Bakar descendant of Al king Al Massoud Youssef”, see figure 9.
- The coin no.5 dates back to the region of the Ayyubid king Al-Kamal, on the face (observe) is written “Allah, No God but Allah, Mohamed is the messenger of Allah, Al-Mansour Al-Mastanser Ballah Amar Al-Mamanen, Minted in Sana'a 600 A.H”, on the back (reverse) is written “The name of Allah, Al king Al-Kamal Abu Al-Maalai Mohamed ibn Al-king Al Adal Abu-Bakar descendant of Al king Al Massoud Youssef”.
- Two coins no. 6 and 7 date back to the region of the Ayyubid king Al-Adal, on the face (observe) of the coins is written “Allah, No God but Allah, Mohamed is the messenger of Allah, Al-Amam Al-Nasser ledeen Allah Ahmed Amar Al-Mamanen, minted in Sana'a 620 A.H”, on the back (reverse) is written “The name of Allah, Al-king Al-Adal Abu Bakar, the descendant of Al-king Al-Kamal Mohamed descendant of Al-King Al-Massoud Youssef”.

By studying the group of coins, It is noticeable that:

- Ayyubids power came to its end by the rise of Rasulids as successors to Ayyubids and the certain of a new Rasulid state in 1228 AD (628 A.H).
- There are many places of mint during Ayyubid period in Yemen, such as Sana'a, Aden, Taiz and Damlah.
- The manufacture processes, figures and inscriptions of the coins are very bad.
- The chemical composition of the coins indicates the decline of economic situation for Ayyubids in Yemen at that period, there isn't enough silver to make their currencies, so they mixed it with copper and lead.

## Conclusions

From the present research the following conclusion can be highlighted:

- The chemical composition of the coins indicates the decline of economic situation for Ayyubids in Yemen at that period and they haven't enough silver to produce their currencies, so they mixed it with copper and lead.
- The coins consist of Ag-based alloy, which mainly consists of silver, copper and lead in a different percentages, this different content played a serious role in deterioration and degradation processes.
- Metallographic and Scanning electron microscope examination results show the occurrence of selective localized corrosion phenomena induced also by the separation of the alloying elements, which creates reactive electrochemical areas.
- Examination results show damaged areas on the surface, the presence of chlorine as an aggressive agent as well as evidence of the chemical reaction between soil constituents and the degradation products.

- XRD data reveal that chlorine also corrodes silver during the archaeological burial in the soil, thus giving rise to the formation of chlorargyrite.
- Corrosion products associated with the coins provide information about the original composition and the environment in which they were preserved, we can deduced that the soil of buried environment is sandy and rich with salts, so it played a dangerous role in the deterioration and degradation processes.

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*Received: January, 09, 2014*

*Accepted: August, 24, 2014*