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AUTHENTICATION AND CONSERVATION OF MARINE ARCHAEOLOGICAL COINS EXCAVATED FROM UNDERWATER OF THE RED SEA, SAUDI ARABIA

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ABSTRACT

The present work aims to develop and establish conservation processes for cleaning marine archaeological silver coins - the Shoiba Hoard Coins in Red Sea, Shoiba Port, near Jeddah, Saudi Arabia. To help the archaeologists study and date these coins, it was necessary to reveal the impeded decorations and the inscriptions on these coins. Before establishing the experimental work to evaluate the selected conservation processes, various tests were performed on different types of the selected coins to assess their statement and condition. XRD analysis was used to characterize the coins. Also scanning Electron Microscope (SEM) attached with energy- dispersive x-ray analyzer (EDX) was used to identify and analyze the corrosion products on the surface of the coins. In this study 5 cleaning methods within various conditions were tested for cleaning the current coins. The efficacy of the combined use of alkaline Rochelle salt and reduction cleaning techniques were evaluated. To evaluate the usefulness of the suggested conservation processes used in this study for cleaning the hoard coins, the coins before, during and after the cleaning processes were investigated by various techniques. SEM with EDAX and XRD techniques were used to characterize the coins after the final conservation. The results showed that the best method that can be used safely and successfully for cleaning of the studied coins is as the following a) initially the corroded coins have to be treated with alkaline Rochelle salt, b) then treated with alkaline dithionite reduction technique or electrolytic reduction technique, finally c) the coins should be rinsed, dried and followed by isolation. The conservation processes developed in this study can be used effectively, safely, and successfully for cleaning of corroded marine archaeological silver coins in this treasure and the simulated marine archaeological coins. The archaeological study of the decorations and inscriptions that appeared on the surface of the coins after their conservation confirms that these coins belong to the Rasulids (Banu Rasul) Dynasty and date back to 1229 to 1454 A.D.

KEYWORDS: Marine Archaeological silver coins, Corrosion products, Conservation processes, Alkaline Rochelle salt, Alkaline Dithionite Reduction Technique, Electrolytic Reduction Techniques, SEM-EDX, XRD

1. INTRODUCTION

Saudi Arabia was located in the centre of the ancient world. So, many trade routes were passing across many regions in Saudi Arabia in ancient times. These trade routes included sea routes such as the Red sea and land routes such as Silk Road. Trade was one of the most popular jobs for most of people in Saudi Arabia during all ancient periods. After Islam, Saudi Arabia becomes a sacred land to which rich Muslims travel to perform Hajj in Mecca. Many Kings and Sultans in various periods tried to hold control over the holy city of Mecca to raise their own prestige. As a result, there is a probability of excavating many different types of coins in archaeological sites in Saudi Arabia. These coins may date back to various civilizations of different periods of history. For instance, these coins may belong to the native people who lived in this region, to traders who came to this region for any reason, or to kings and Sultans who ruled this region in various periods.

Archaeological coins are important findings that provide the archaeologists with valuable information revealed by written documents that come in forms of effigies, short inscriptions, and symbols (Reale, et al, 2012). During the Islamic periods, coins were one of the most important and lasting signs that Sultans, Caliphs, and Kings took care to mint once they start ruling. Once a ruler was appointed, he would order minting of coins with his name and nickname written on them. Science coins are considered as signs of economic growth and sources that chronical important political events such as crowning and excommunicating kings and Sultans. (Yonis, 2016).

The Rasulids (Banū Rasūl) ruled Yemen from 1229 to 1454 A.D. Umar bin Ali was the first sultan of the Rasulid dynasty. While Hijaz, a region in the west of present-day Saudi Arabia, fell under the Mamluk Sultans of Egypt, the Rasulids temporarily held control over the holy city of Mecca, accordingly raising their own prestige. The Rasulid era is often considered as one of the most brilliant era in the history of Yemen. In Rasulids kingdom there were many towns, castles, and an excellent port. Kings and Sultans of Rasulids kingdom, as all kings in Islamic periods, were interested in producing coins which included their names, nicknames, and towns of producing coins (Rasulid dynasty, 2015, Alaroussi, 2010, Vallet, 2006, Saeed, 1997).

Although silver is generally little susceptible to corrosion, archaeological silver coins (that contain a substantial amount of copper such as our case study, or another alloying element) are easily damaged and corroded (Viljus, and Viljus, 2013). These silver coins were subjected to various corrosion processes resulting in different corrosion products that gradually alter their aspect, shape, nature, and resistance (Al-Saad and Bani-Hani, 2015, Ioanid, et al, 2011). Silver coins actually consist of alloys with other metals, partly to make the alloy harder and also to economize the amount of silver used. In general, the most commonly employed alloys used to produce coins are: the so called "sterling silver" (92.5% Ag, 7.5% Cu), "coin silver" (90% Ag, 10% Cu), and eutectic or brazing alloy (71.9% Ag, 28.1% Cu), (Costa, 2015). When coins are recovered from the sea, especially warm areas such as the Red sea, they are commonly encrusted with thick layers of calcium carbonate, magnesium hydroxide, metal corrosion products, sand, clay, and various forms of marine life such as shells, coral, barnacles, and plants. Thick encrustations form around the coins undergo considerable attack by sulfate reducing bacteria. Accordingly, the most commonly encountered corrosion products on silver and silver alloys in a marine environment are silver sulfide Ag_2S and silver chloride AgCl. Both compounds are stable mineral forms that do not take part in any further corrosive action with the remaining silver. Silver chloride, is generally not extensive on silver artefacts recovered from the salt water; only some silver coins recovered from the sea are superficially enriched in AgCl. In the marine environment, with its abundance of soluble sulfates and organic matter that decomposes and consumes oxygen, the sulfate-reducing bacteria utilize the available sulfate under anaerobic conditions to form hydrogen sulfides as a metabolic product. The hydrogen sulfide in turn reacts with silver and silver alloys to form silver sulfide, Ag_2S, by far the most common mineral alteration compound of silver. A significant percentage of silver artefacts is completely converted to sulfides. The sulfide surface layer disfigures the surface details such as inscriptions, marks, and stamps (Dillmann, et al, 2013).

Base silver alloys with copper, however, differ because copper corrodes preferentially and forms cuprous chloride which continues to corrode the copper component of the silver alloy coins. In these cases the silver is treated as if it were copper (Wanhill, 2005). In a marine Environment, cuprous chloride and cuprous sulfide are the most common corrosion products of copper. CuCl (cuprous Chloride), $CuCl_2$ (Cupric Chloride), Cu_2O (Cuprous Oxide), and the aesthetically pleasant green and blue colored cupric carbonates [$Cu_2(OH)_2CO_3$] (Malachite), and [$Cu_3(OH)_2(CO_3)_2$] (Azurite) are the most corrosion products identified on copper objects. In sea water copper is often converted to cuprous and cupric sulfide, Cu_2S and CuS, by the action of sulfate-reducing bacteria. When the marine encrustations are removed, copper and cupreous artefacts may be covered with a black powdery of copper sulfide of different thickness which imparts an unpleasant appearance. The copper sulfide layer does not adversely affect the object after recovery from the sea like the copper chlorides; they disfigure the object affecting its shape and size. The sulfide corrosion is easily removed and does not cause major trouble for the conservators (Dillmann, et al, 2013). To establish any appropriate conservation process for coins, it is necessary to estimate the statement of the coins as well as to investigate and analyze the chemical compositions and the corrosion products on the surface of these coins (Abdel-Kareem, et al, 2011). Many efforts have been done to investigate, understand, and analyze the corrosion products on metals and to explain the mechanisms of the corrosions on the metals (Abdel-Kareem, et al, 2016, Wan, et al, 2015, Mousser, 2011, Rodrigues, et al, 2011, Beck, et al, 2008, Nord, et al, 2005, Ingo, et al, 2004, MacLeod, and Schindelholz, 2004, Ullén, et al, 2004).

Silver coins recovered from marine sites are very unstable and must be treated to prevent irreversible deterioration (Hamilton, 1999). The reasons to treat silver coins are to remove disfiguring corrosion layers to reveal details, for aesthetic reasons, to reduce mineral products back to a metallic state, and to remove the chlorides from the copper component part of base silver alloys (Hamilton, 2015, Hamilton, 2011). However, it should be kept in mind that corrosion products existing at the surface can act as a barrier for further reaction with the environment, and that their removal therefore makes the object more reactive (Coasta, 2015). As a result, the choice of cleaning method for a particular object has to be assessed carefully by conservators in terms of risk and benefit to the object, as no method currently in use is 100% successful. A large part of archaeological silver coins only needs slight treatment. In most cases, corrosion products can be removed with a simple chemical solution (Viljus, and Viljus, 2013). Not all conservators agree on specific conservation processes for cleaning of coins. For example, some studies mention that chemical cleaning methods are not easily controlled and can be unpredictable, usually resulting in the loss of the original surface. Air abrasive, whilst useful, is often difficult to control and can produce a matt surface. Mechanical cleaning can take a long time and damage can occur either through breakage due to pressure applied to the object or scratching of the surface (Hamilton, 2015). Efforts which have been done on conservation of coins should be considered (Abdel-Kareem, 2015, Hamilton, 2015, Novakovic, et al, 2013, Viljus, and Viljus, 2013, Hamilton, 2011). Costa (2015) reviewed the historic evolution of cleaning procedures concerns silver alloyed with different elements, especially copper. As a conclusion, he confirmed that although the evolution in this area has been positive, an important point remains to be developed further. It concerns co-operative research between restorers and scientists whose main goal would not be the discovery of a new procedure or formula, but a real understanding of the consequences of using given products or applying certain techniques (Costa, 2015).

The conservation of coins excavated from a marine site, especially warm areas such as the Red Sea, is not very similar to the conservation problems presented by coins from most land sites (Abdel-Kareem, 2015). Although there are many studies done on the processes used in conservation of silver metals, there are rare ones on marine coins especially those discovered from underwater of the Red Sea. For that reason, more efforts are still needed to conserve these coins. The method used for cleaning a coin is chosen according to the type of the corrosion products and condition of the coin. Most of these methods are commonly used separately. Only the mechanical methods are commonly used prior the other methods for cleaning of silver coins.

This study aims to evaluate the efficacy of the combined use of alkaline Rochelle salt and reduction cleaning techniques for cleaning marine archaeological silver coins excavated in hundreds or thousands of coins such as Shoiba silver coins treasure in Red Sea, Shoiba port, near Jeddah, Saudi Arabia The developed method was applied in conservation of the selected coins from this treasure. It can be used in conservation of any other simulated marine archaeological coins. Also, the study aims to authenticate the conserved coins according to the revealed writings and descriptions on the surface of these coins.

2. EXPERIMENTAL

2.1 Discerption of the studied coins

The studied coins are called shoiba hoard coins, excavated from under water of the red sea, shoiba port, near jeddah, saudi arabia. This treasure contains about 5 thousands of silver coins. These coins were discovered from seven years ago. They were separated from each other. After their separation, the coins were stored in distilled water in conservation lab. Of the saudi commission for tourism & antiquities, riyadh, until their treatment and conservation in the current work (see figure 1). Unfortunately there are not documented information about the method used in separating these coins.

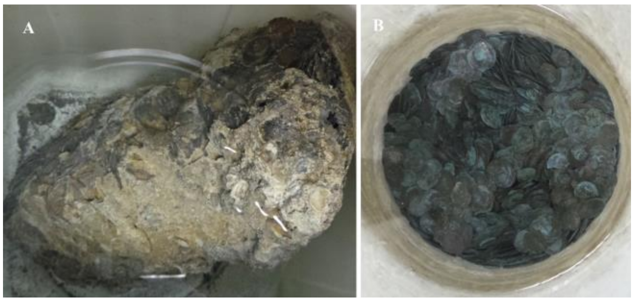

Figure 1. Part of the hoard coins, A) one mass of the coins before any treatments, B) Part of the coins after separating and keeping them in distilled water until their treatments in the current work.

2.2 The characterization and status of the studied coins.

To characterize and estimate the condition status of the studied coins and to identify types of the corrosion products covered with a layer of corrosion products (in different colors, black, light blue to blue-green) covering their surfaces, various investigation and analysis methods were carried out on the coins. The coins were investigated visually and microscopy. The Scanning Electron Microscope with Energy dispersive X-ray Analysis (Model JEOL JSM-6510LV, voltage 30 kV) has been used according to Abdelkareem, 2015, to examine the surface morphology of the selected coins. For EDAX analysis, 15 selected coins were investigated to provide us with the average of the identified elements on the investigated coins. Also, the coins were analyzed with X-ray diffraction (XRD) to identify the component of the coins and the corrosion compounds that disfigured the surface. This analysis was carried out on Philips X-ray diffraction, type PW 1840, giving 40 KV, Cu Kα radiation at 25 mA, the scanning range of 2θ was from 5 to 60° and the scanning speed was 2°/min. The samples were prepared and investigated according to Abdel-Kareem (2015).

2.3 Conservation processes

Five selected conservation methods were chosen according to their effectiveness and their suitability to be applied in the conservation laboratory, Saudi Commission for Tourism & Antiquities, Riyadh. The 5 tested methods are alkaline Rochelle salt (method 1), alkaline dithionite reduction technique (method 2), electrolytic reduction technique (method 3), alkaline Rochelle salt + alkaline dithionite reduction technique (method 4), and alkaline Rochelle salt + electrolytic reduction technique (Method 5). All tested cleaning methods were carried out on the coins without mechanical cleaning. Various conditions such as various periods and different concentrations for each method were evaluated.

2.3.1 *Alkaline Rochelle salt*

Rochelle salt was prepared by dissolving 50gm of sodium hydroxide NaOH in every liter of cold water. Then 150 gm of sodium and potassium tartrate was added to this solution and was completely dissolved by good stirring. The prepared solution was stored in bottle until its use. The coins were immersed in the prepared solution to dissolve cupper corrosions products which changed the color of the solution to blue. The solution was changed from time to time until this blue color stopped. During the immersing of coins, a smooth brush was used to brush the coin's surface to help dissolve rust components. Also, between every change of solution, the coin's surface was rinsed and brushed under water to remove any disintegrated rust. Then, it was rinsed and cleaned again with water.

2.3.2 *Alkaline Dithionite Reduction Technique*

The Dithionate solution was prepared according to Abdel-Kareem 2015. The tests were done on both coins that were not prior cleaned with alkaline Rochelle salt method and coins that were prior cleaned with it. The tests were done in separate processes. First, the coins were immersed in a 10% hydrochloric acid solution for 10 minutes in order to remove any remaining calcifications. These coins were rinsed well with running water. Then, the coins were immersed in dithionate solution in a closed glass bottle. The glass bottle was closed and shook well to ensure that the solution was mixed well and that it covered all coins' surfaces. After nearly one hour, the coins were taken out and rinsed well with water to remove any remaining corrosion products from their surfaces. If the cleaning degree was not enough, we changed the dithionate solution and repeated the process again. After repeating this process many times, the coins were taken out and washed well with distilled water. Then, they were polished with sodium bicarbonate and rinsed well in non-ionized water for more than 48 hours to remove any effects of treatment solutions. After that, they were dried and kept until carrying out any other treatment.

2.3.3 *Electrolytic Reduction Technique*

Electrolytic reduction cleaning tests were done on both coins that were not prior cleaned with alkaline Rochelle salt method and coins that were prior cleaned with it. Special electrolytic reduction cleaning process was stablished according to Abdel-Kareem, 2015. An electric current with current intensity that ranged between 0.3-0.5 A/cm^2 and voltage that ranged between 8-10V was connected. In this method the stainless steel No.316, was used as anode. Each one of the coins was hanged on the holder wire (Cathode). Then, it was immersed in the 5% formic acid solution in a glass bottle. One surface of the coin was facing the anode. The process was continued for different periods until a suitable degree of cleaning of the coin was achieved. It was noticed that the suitable cleaning period for coins was 3 minutes for each surface, but in some coins that were covered with more corrosion products, this period was extended according to the thickness of this rust layer. After reaching a suitable result of cleaning, we removed the coins from the formic acidic solution while the DC is working. Then, the coin was turned, so that the other surface of it would face the anode. By this way, we were able to clean both surfaces in the same efficiency. After that, the coin was immersed again in the acid solution and the previous steps were repeated. Then, the coin was removed from the solution while the DC is working. After getting the coins out of the connecting solution, the coins were washed and cleaned in distilled water with soft brush. Then, the treated coins were polished and gentle rubbing with baking soda (sodium bicarbonate). Cleaning with baking soda is effective, because its particles are not hard enough to scratch the metal surface, but are still abrasive enough to remove the softened corrosion products. The cleaned coins were rinsed well in non-ionized water for more than 48 hours to remove any effects of treatment solutions. After that, they were dried and kept until carrying out any other treatment.

2.4 Evaluation of the tested conservation processes

For evaluating the conservation status of the conserved coins, the coins were investigated before, during, and after the conservation processes visually and microscopy. Also EDAX and XRD were used to investigate the coins. All investigation methods were carried out as described above.

3. RESULTS AND DISCUSSION

3.1 The characterization and status of the studied coins

The visual investigation of the studied coins showed that the coins were completely covered with a layer of corrosion products that blurred all inscriptions and decorations found on these coins. The maximum width of these coins is about 27 mm, their thickness ranged to 1mm, and their weight is about 182 mgr. The coins were covered with a thin layer of corrosion products (in different colors, black, light blue to blue-green) (see figure 2). It was clear that most of corrosion products on the surface of the coins were corrosion products of copper and silver. This indicates that these coins are made of silver alloy that contain silver and copper in their components. It may be according to the unfavorable conditions surrounding of the coins, the copper may be leaving the coins and immigrate to behind the surface of the coin. Copper is an active metal that can react with different elements (O, Cl, S, etc) that are present in the environment surrounding the coins to produce aggressive corrosion products. The results show that the coins become brittle and more fragile. The shape of the coins are eroded and it is clear that an unusual erosion corrosion phenomenon is found on many of the coins. Their aspect was so distorted that no detail of the original surface could be retrieved. The corrosion layer covers the surface but does't completely hide the surface details, such as inscriptions, marks, and stamps. The effects of corrosion and embrittlement appeared clearly on these coins.

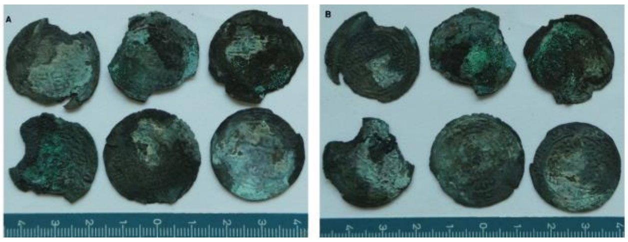

Figure 2 Example of photos that show the condition of the studied coins from 2 sides.

Results of SEM morphological examination for coins before the cleaning were presented in figure 3. The results show that the coins were covered with a layer of corrosion products mixed with marine deposits that disfigured it, hid their surface, figures and inscriptions, and made them ugly. This composite layer can be seen clearly under SEM investigation. The results show that these coins suffered from severe weakness and were covered with a large rust layer. The surface pattern appears heterogeneous, coarse, disparate, and covered with crystals compounds such as calcite and sands.

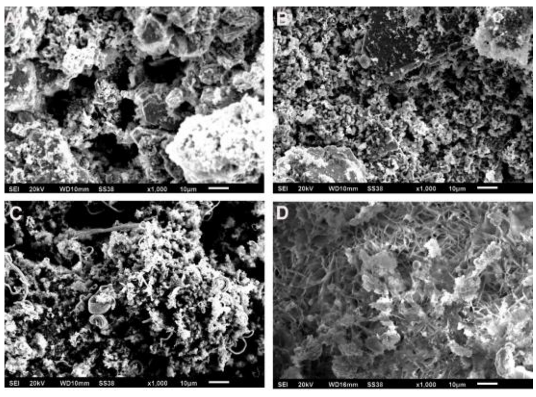

Figure 3 SEM images show examples of the studied coins before the cleaning.

The results of XRD (Fig. 4) of the coins before any treatment indicate that the coins are made from alloy which is made from silver (Ag), and copper (Cu). The results show that most of the corrosion products commonly presented on copper and silver were identified. The results also show that the corrosion products identified on the coins contained various types of copper and silver corrosion products. The identified corrosion products are: Chlorargyrite AgCl which is in white color, Acanthite Ag_2S which is in black color, Brochantite $CuSO_4$ which is in black color, and Covellite Cu S which is in black to grey color. The identified corrosion products consist mainly of copper (II) carbonates [$Cu_2CO_3(OH)_2$] Malachite in green color, Copper (II) oxide, (Cu O) Tenorite in a black corrosion layer, Paratacamite [$Cu_2(OH)_3Cl$], Nantokite CuCl in green color, Copper oxide (Cu_2O), Cuprite in reddish color, Atacamite [$Cu_2(OH)_3Cl$], Azurite [2cu co_3.cu$(OH)_2$] Silver (I) Chloride, Metallic Copper (Cu) and Metallic Silver (Ag).

The current study suggests that the corrosion products on the coins may be formed because the treasure was embedded in salt water of the Red Sea. This soil might contain contaminations active ions such as S and Cl. The types of corrosion indicated that both electro and chemical corrosion processes were carried to corrode the coins during their impediment in the salt water. In the case of silver alloys with significant amounts of copper, the copper will corrode preferentially and form cuprous oxide, cupric carbonate, and cuprous chloride. As a result, the following compounds were identified. Corrosion of Chlorides components such as Nantokite CuCl, Paratacamite Cu_2 $(OH)_3Cl$, Atacamite $Cu_2(OH)_3$ Cl, Botallckite $Cu_2(OH)_3Cl$, which are green, were identified. This may be due to the chemical reaction between the Cl ion in the sea water and the copper in the component of the coins during their staying under the water of the Red Sea. These corrosion products are the most dangerous corrosion on the copper. Also the present of the Chlorargyrite AgCl may be due to the reaction between the Cl ion in the sea water and the silver component in the coins while their staying under the water of the Red Sea.

Corrosion products of sulfites such as Acanthite Ag_2S, Brochantite $CuSO_4$, and Covellite CuS in grey-black color, were identified. This may be due to the abundance of soluble sulfates as a metabolic product in the water of the Red Sea. All these results agree with the results obtained by Hamilton, 1999, who confirm that in a marine environment, with its abundance of soluble sulfates and oxygen-consuming, decaying organic matter, sulfate-reducing bacteria utilizes available sulfates under anaerobic conditions to form hydrogen sulfides as a metabolic product. The hydrogen sulfide reacts with the silver to form silver sulfide. Most marine-recovered silver artifacts have a thin sulfide surface layer which has removed some surface details, such as inscriptions, marks, and stamps. A large percentage of the artifacts, however, are completely converted to sulfide; others have only minimal metal remaining.

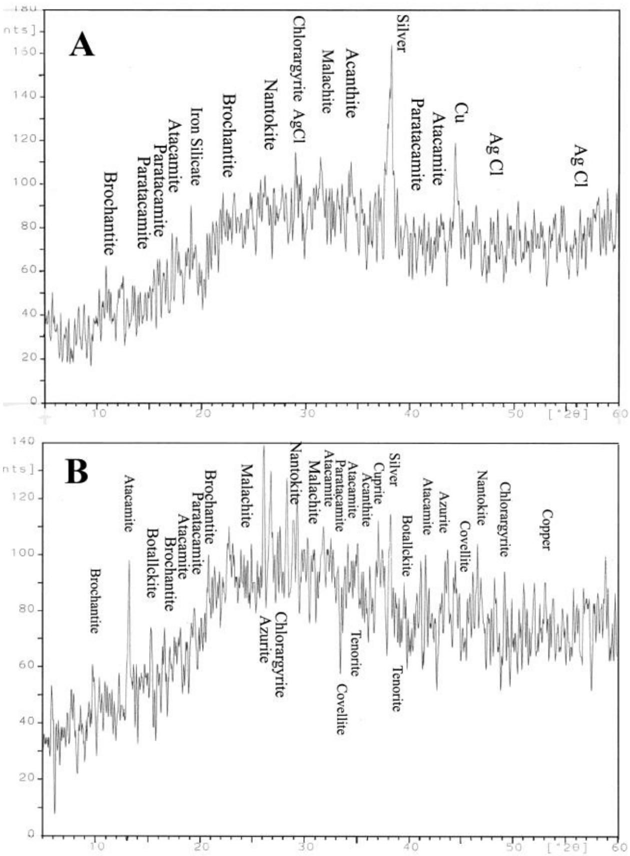

Figure 4. Analysis for one of the coins by using XRD; it identifies the most important rust compounds found on this coin's surface.

The results of EDAX analysis of the studied coins before the cleaning are shown in table 1 and figure 5. The results of the EDAX analysis for the corrosion layer of the coins (in green/blue color) indicate that the contamination elements such as Cu, O, C, Al, S, and Fe are identified. The results show the presence of Cu, O and C as major elements and Fe, S, and Al as minor elements. These results confirm that the corrosion layer consists mainly from copper corrosion products. The results also show that the main component of the corrosion products on the surface of the coin is copper (Cu), about 49%. The results of the corrosion layer of the coins (in black color) indicate that there is sulfide surface layer. This explain why the details of the inscriptions and symbols on the surface were hidden. As the sulfide surface layer is black and opaque layer. Results that were taken from both SEM-EDAX and XRD showed that these corrosion components were the common ones that are usually found on the coins of silver alloys with significant amounts of copper, excavated from a marine environment, with its abundance of soluble sulfates and oxygen-consuming, decaying organic matter, sulfate-reducing bacteria utilizes available sulfates under anaerobic conditions to form hydrogen sulfides as a metabolic product, such as our case study from under water of the Red sea.

Table 1 The EDAX analysis of the chemical composition (Weight %) of coins before any cleaning.

Element	Green colour		Black colour	
	Mean	SD	Mean	SD
C	9.65	1.38	7.44	2.45
O	34.82	6.27	36.57	1.89
Mg	0.02	0.07	0.06	0.11
Si	0.28	0.27	0.16	0.14
P	0.18	0.16	1.02	0.47
S	0.53	0.43	4.28	1.02
Cl	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00
Ca	0.40	0.09	0.74	0.19
Fe	0.00	0.00	0.81	0.57
Cu	49.34	8.55	13.80	3.86
Zn	1.65	0.41	0.63	0.57
Ag	3.13	2.67	34.43	2.50

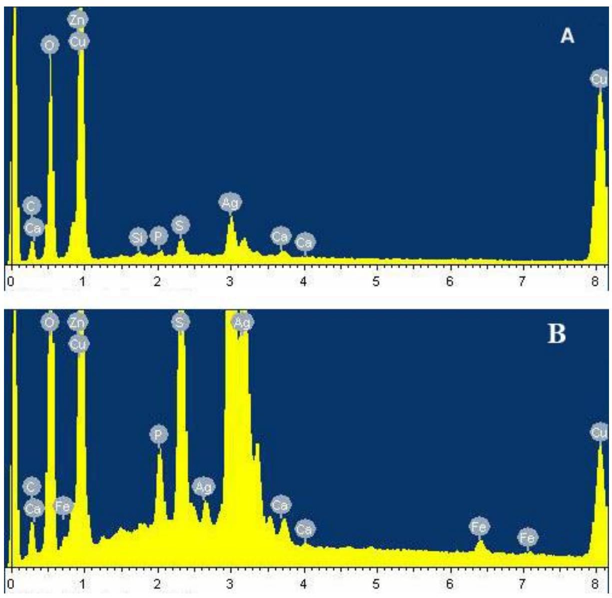

Figure 5. The EDAX analysis of the chemical composition (wt. %) of the studied coins before any treatment A) Green, B) Blue, C) Black.

3.2 Conservation processes

3.2.1 Visual Observation. The results of visual observation of surface of the coins after the cleaning treatment were abstracted in able 2 and Figure 6. The results showed that the corrosion layer was partially removed from the coins treated with alkaline Rochelle salt, but the writings, inscriptions, and decorations were still invisible. This was because this treatment was not able to remove the silver chloride and the sulfide surface layer that covered the writings, inscriptions, and decorations which made them invisible. This indicate that alkaline Rochelle salt technique is not harmful for this kind of coins, but it is not effective for cleaning them.

Although the corrosion layer, the silver chloride and the sulfide surface layer, was removed from the coins treated with electrolytic reduction technique (without prior treatment with alkaline Rochelle salt), the salmon-pink stains appeared on the surface of the coins. Therefore, the surface of the coins was distorted. The results showed that the coins became more shiny but with strong yellow tint. This indicate that electrolytic reduction technique is a quite effective method for removal of the corrosion layer, but it cannot be recommended for coin silver alloyed with copper (such as our case coins), because there is sometime a risk of plating a layer of element copper on the surface.

The corrosion layer, the silver chloride and the sulfide surface layer, was removed from the coins treated with alkaline dithionite reduction technique (without prior treatment with alkaline Rochelle salt). However, a thin light purple layer was formed on the surface of the coins and it was difficult to remove it. Therefore, the surface of the coins was distorted. This indicate that alkaline dithionite reduction technique is a quite effective method for removal of the corrosion layer, but it cannot be recommended for coin silver alloyed with copper (such as our case coins), because there is sometime a risk of plating a layer of element copper on the surface.

The results show that the corrosion layer, the silver chloride and the sulfide surface layer, was removed well from the coins treated with alkaline Rochelle salt + alkaline dithionite reduction technique. The treatment with this method has given coins more or less natural appearance (as one would expect from silver coins). The condition of these coins became good with writings and inscriptions appeared clearly on their surfaces.

The results show that the corrosion layer was removed well from the coins treated with alkaline Rochelle salt + electrolytic reduction technique. This method softened the corrosion layer that help the treatment with baking soda to remove the softened corrosion layer. The coins surfaces became in good condition; they became sleek and homogeneous. The condition of these coins became good and the writings and inscriptions appeared clearly on coins' surfaces.

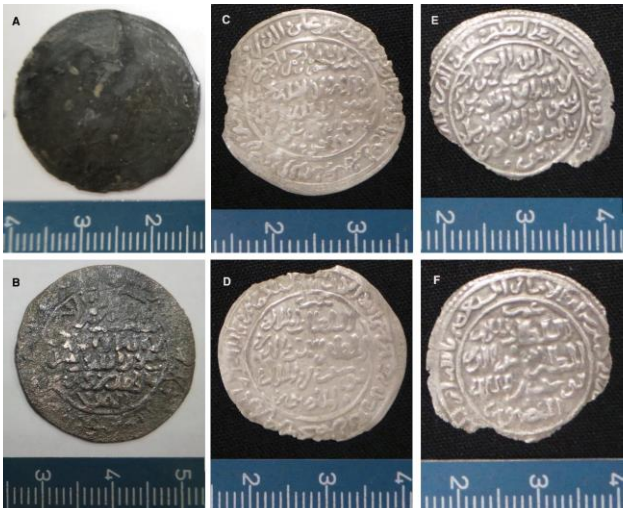

Figure 6. Example Photos show the condition of the studied Islamic marine archaeological coins after the cleaning

Table 2 The visual observation of all conservation methods used in this study

	Conservation Process	Results
1	Alkaline Rochelle Salt	Partially effective
2	Alkaline Dithionite Reduction Technique	Not good
3	Electrolytic Reduction Technique	Not good
4	Alkaline Rochelle Salt + Alkaline Dithionite Reduction Technique	Effective
5	Alkaline Rochelle Salt + Electrolytic Reduction Technique	Effective

***3.2.2 SEM Examination*:** The results of SEM of the coins after the treatments with the suggested methods (Figure 7), confirm the obtained results by visual observation that show that Rochil Salt technique was effective in removing large amounts of corrosion products that could be removed by Rochil salt technique such as copper corrosion products, but still there was a layer of corrosion covering the coins. This layer of corrosion disfigures all details, inscriptions, and symbols on the surface of coins. These corrosion components may include sulfide surface layer and silver chloride. In order to remove these corrosion products, the other treatments were used as well. The surface of the coin after the treatment was still rough and the corrosion products covered the surface. The results show that both methods 2 and 3 are not good for removing all corrosion products on the coin surface. For example, in figure 8 B it is clear that the surface is still covered with corrosion layer. After the treatment with the method 4 (alkaline Rochelle salt + alkaline dithionite reduction technique) and method 5 (alkaline Rochelle salt + electrolytic reduction technique), the surfaces of the coins became in good condition; they became sleek and homogeneous. The results showed that all corrosion products were removed from the coins. The appearance of the coins treated with both method 4 and method 5 showed that these coins were made up mainly from silver.

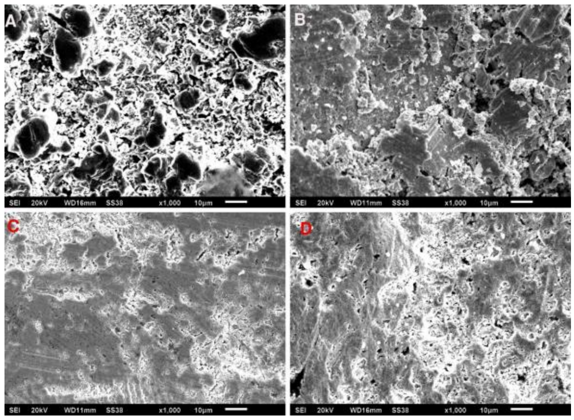

Figure 7. Microphotos taken by scanning electron microscope for one of the coins after the cleaning

***3.2.3 EDAX Examination*:** The results of EDAX analysis of the coins after the treatment were shown in tables 3-5. The results show that the coins treated with method 1 (alkaline rochelle salt) reduce most of the contamination elements but doesn't remove all of them. The contamination elements such as Cu, O, C, Al, and S, are still present. This result confirmed that the corrosion layer was partially removed from the coins after the treatment. However, the percent of silver is increased to reach about 52 %. This indicate that alkaline rochelle salt technique is not harmful for this kind of coins but it is not effective for cleaning them.

The results of the EDAX analysis confirm that all corrosion products on the coins treated with method 4 (alkaline rochelle salt + alkaline dithionite reduction technique) and method 5 (alkaline rochelle salt + electrolytic reduction technique) were removed. The percent of the silver in the coins after the final cleaning raise up to about 93% to 95% while the percent of the silver in the coins before any treatment was from 3% to 34%. This confirm that all corrosions elements such as Mg, Si, P., S., Cl, K., Ca, Fe, and Cu were removed.

These results confirm that method 4 (alkaline rochelle salt + alkaline dithionite reduction technique) and method 5 (alkaline rochelle salt + electrolytic reduction technique), are effective in cleaning of the marine silver coins.

Table 3 The EDAX analysis of the chemical composition (Weight %) of the coins after the chemical cleaning.

Element	Mean	SD
C	28.12	8.50
O	10.01	4.50
Al	1.60	1.20
Mg	0.03	0.10
Si	0.48	0.19
S	7.32	2.30
Ca	0.73	0.24
Ag	52.85	6.54

Table 4 EDAX analysis of the chemical composition (Weight %) of the coins after the Dithionate Technique.

Element	Mean	SD
C	2.22	0.62
O	3.27	2.03
Ag	95.71	3.01

Table 5 EDAX analysis of the chemical composition (Weight %) of the coins after the Electrolytic Reduction Technique.

Element	Mean	SD
C	3.61	1.17
O	3.68	1.28
S	0.47	0.09
Ca	0	0
Ag	92.59	2.50

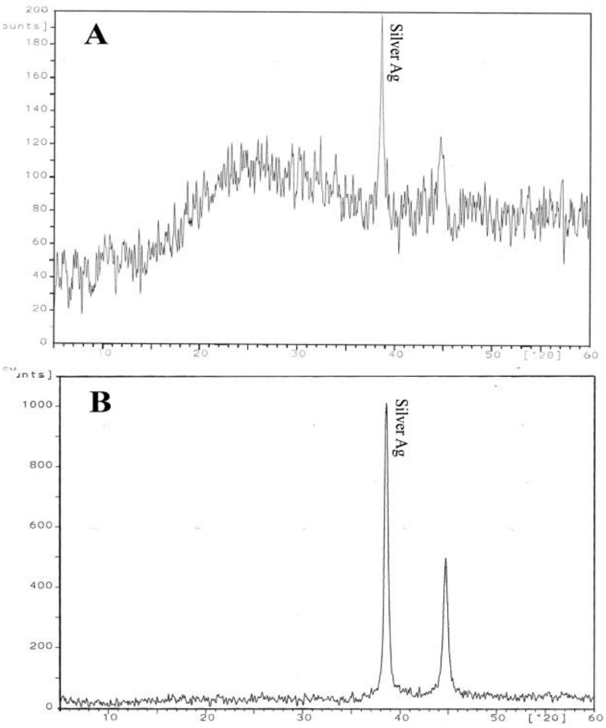

Figure 8. XRD analysis for a coin after the cleaning

3.2.4 XRD Examination: The results of XRD confirm that the corrosion layer was partially removed from the coins treated with alkaline Rochelle salt. The percent of silver was increased. This indicate that alkaline rochelle salt technique is partially good for cleaning of the selected coins but it is not effective for cleaning them well.

The results of the XRD analysis confirm that all corrosion products on the coins treated with method 4 (alkaline rochelle salt + alkaline dithionite reduction technique) and method 5 (alkaline rochelle salt + electrolytic reduction technique) were removed (see figure 8). These results confirm that method 4 (alkaline rochelle salt + alkaline dithionite reduction technique) and method 5 (alkaline rochelle salt + electrolytic reduction technique), are effective in cleaning of the marine silver coins.

4. APPLICATION PART

The developed method (alkaline Rochelle salt + electrolytic reduction technique) as mentioned above was applied for cleaning the selected coins. In the beginning the corroded coins were treated with alkaline Rochelle salt. Then they were treated with electrolytic reduction technique. Then the coins were treated with baking soda to remove the softened corrosion layer. The coins' surfaces became in good condition; they became sleek and homogeneous. Following the final cleaning, the coins were rinsed with de-ionized water. After the rinsing process, the coins were dried with dehydrated in acetone. Protective coatings are often applied to metal objects to prevent or reduce the possibility of corrosion from high humidity, frequent handling, and atmospheric pollution. However, the selected coating should not be harmful for the coins. In this study the coins were coated with a clear acrylic lacquer of Palaroid B72. The solution of Palaroid B72 was used in 4% solved in acetone. The coins were dried and stored in a closed cabinet in RH less than 30%. This was to prevent the deterioration of the coins until their display or storage in the museum. By using this method we conserved 1500 coins that were used in the archaeological part in this study (see figure 9).

Figure 9. Samples of coins after the final treatment

5. ARCHAEOLOGICAL STUDIES FOR THE TREATED COINS

For authentication of these coins, it was important to read all decorations, inscriptions, and writings on their surfaces. After the final treatment of the coins, different inscriptions, figures and, writing words appeared on the surfaces. The archaeological studies for the writings and inscriptions on the surfaces of these coins confirm that these coins belong to Rasulids (Banū Rasūl) dynasty that ruled in Yemmen from 1229 to 1454 A.D. These writings that were written in Arabic words show different names and nicknames of kings or Sultans of Rasulids (Banū Rasūl) dynasty.

The results of analysis and investigation of the coins show that they are made from silver. This result confirms that the type of the studied coins are Dirhams. Dirham in Islamic periods was made from silver, and it was equal to a quarter-dinar (Al-Khazraji, 1983, Ibn Aldiba, 1983, Currency and Islamic Coins, 2015). Kings and Sultans who were identified and read on these coins are al-Sultan al-Malek al-Muzaffar Shams al-Din Yusuf Bin al-Malek al-Mansur Omar, al-Sultan al-Malek al-Mu'ayyad Hazber al-Din Da'ud Bin al-Malek al-Muzaffar Yusuf, and al-Sultan al-Malek al-Mujahid Saif al-Islam Ali Bin al-Malek al-Mu'ayyad Da'ud. Also, writings and inscriptions on these coins show many of the places used in producing dirhams. These places include Zbid, Adan and Al-Mahgam.

The names of the Sultans and towns as well as the dates that were identified on these coins agree with the information data about Rasulids (Banū Rasūl) dynasty in Yemen that ruled from 1229 to 1454 A.D. that mentioned in the references (Saeed, 1997, Vallet, 2006, Alaroussi, 2010, Rasulid dynasty, 2015).

Discovering these coins from under the Red Sea water, Shoiba Port, Near Jeddah, Saudi Arabia confirms that the ancient trade route during the Rasulid dynasty that ruled Yemen, may be passing across this port while the travel of the ships from Adan Port in Yemen to the Egyptian cities. As the historical data that we obtained in the references mention that the old trade route in Islamic periods extended from the far East and Indian Ocean in the Yemeni city of Aden to the Red Sea to the Egyptian cities associated with European traders and private dealers in Italian cities who carry goods flowing via this route to Europe; this road was the most active during Rasulids (Banū Rasūl) dynasty who ruled in Yemen from 1229 to 1454 A.D. (Ibn Aldiba, 1983, Al-Khazraji, 1983, Saeed, 1997, Alaroussi, 2010).

Figure 10. Example of coins belonging to al-Sultan al-Malek al-Muzaffar Shams al-Din Yusuf Bin al-Malek al-Mansur Omar

Figure 11 an example of coins belong to al-Sultan al-Malek al-Mu'ayyad Hazber al-Din Da'ud Bin al-Malek al-Muzaffar Yusuf

Figure 12 an example of coins belong to al-Sultan al-Malek al-Mujahid Saif al-Islam Ali Bin al-Malek al-Mu'ayyad Da'ud

6. CONCLUSION

Although alkaline Rochelle salt is not able to completely remove all corrosion compounds on marine archaeological silver coins, it is considered an important process that should be done prior any other cleaning methods. Alkaline Rochelle salt technique is not harmful for this kind of coins but it is not effective in cleaning them.

Electrolytic reduction technique (without prior treatment with alkaline Rochelle salt) is a quite effective method for removal of the corrosion layer, but it is not recommended for coin silver alloyed with copper (such as our case coins), because there is sometime a risk of plating a layer of element copper on the surface of the coin. This layer of the copper alter the color of the coin and it is too difficult to remove.

The developed method, alkaline Rochelle salt + alkaline dithionite reduction technique (method 4), or alkaline Rochelle salt + electrolytic reduction technique (Method 5), is effective for cleaning of marine archaeological silver coins (Shoiba Hoard Coins). The coins' surfaces treated with any of them became in good condition; they became sleek and homogeneous, and the writings and inscriptions appeared clearly on coins' surfaces.

The best method that can be used safely and successfully for conservation of marine archaeological silver coins (Shoiba Hoard Coins) is as the following. In the beginning the corroded coins have to be treated with alkaline Rochelle salt. Then they should be treated with alkaline dithionite reduction technique or electrolytic reduction technique. Following the final cleaning, the coins have to be rinsed with de-ionized water. After the rinsing process, the coins have to be dried well. Finally after finishing the treatments, the coins have to be isolated and coated with a clear acrylic lacquer such as Palaroid B72.

The conservation processes developed in this study can be used effectively, safely, and successfully for cleaning of corroded marine archaeological silver coins in this treasure and the simulated marine archaeological coins.

The archaeological study of the decorations and inscriptions that appeared on the surface of the coins after their conservation confirms that these coins belong to the Rasulids (Banu Rasul) Dynasty and date back to 1229 to 1454 A.D.

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